

**LABORATORY STUDIES ON THE MANGANESE - SULPHUR
INTERACTIONS IN THE BLAST FURNACE IRON IN THE
TEMPERATURE RANGE OF 1200 TO 1400°C**

by
PRAVEEN KUMAR

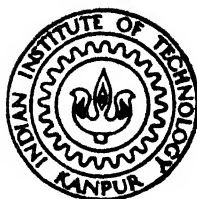
ME

1986

M

KUM

LAB



**DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
KANPUR**

DECEMBER 1986

7 201 001
CENTRAL
08055

ME-1906-M-KUM-LAB

CERTIFICATE

Certified that the work reported in : is thesis entitled 'Laboratory Studies on the Manganese-Sulphur Interactions in the Blast Furnace Iron in the Temperature Range of 1200 to 1400°C' by Praveen Kumar has been carried out under my supervision and has not been submitted elsewhere for the award of degree.

(N.K. BAIRA)
Department of Metallurgical Engg.
Indian Institute of Technology,
Kanpur

December ,1986.

ACKNOWLEDGEMENTS

The author would like to express his sincere and foremost gratitude to Dr. N.K. Batra for patiently guiding me through all the steps involved in the planning, execution and completion of the present work.

He would also like to thank Mr. D.P. Tripathi, Mr. A. Sharma and Mr. S.C. Chaurasia for their help and cooperation.

The author would not like to forget his laboratory inmates viz. Mr. Pankaj Mittal, Mr. Prashant Sagar, Mr. Binod Kumar and Mr. V. Srinivasan who were ever ready with their assistance when-ever required.

Lastly, the author would like to thank Mr. Shyam Ji Gupta for typing out the manuscript and Mr. V.P. Gupta for his assistance in the drawings.

Praveen Kumar

(PRAVEEN KUMAR)

TABLE OF CONTENTS

	<u>page</u>
LIST OF TABLES	(v)
LIST OF FIGURES	(vi)
ABSTRACT	(vii)
CHAPTER I INTRODUCTION	1
1.1. Importance of Sulphur Control in Steel	1
1.2 Origin of Sulphur in Steel	1
1.3 Control of Sulphur in Steel	2
1.4 External Desulphurisation	3
1.5 Scope of the presentwork	4
CHAPTER II LITERATURE SURVEY	5
2.1 Activity of Sulphur in Liquid Iron Alloys	5
2.2 Slag-Metal Equilibrium	13
2.3 Departure from Equilibrium in Blast Furnace	21
2.4 Effect of Manganese on Desulphurisation	23
CHAPTER III PLAN FOR PRESENT WORK	25
CHAPTER IV EXPERIMENTAL DETAILS	27
4.1 Equipments	27
4.2 Materials	31
4.3 Experimental Procedure	35
CHAPTER V RESULTS	40
5.1 Analysis of Original Rourkela Steel Plant Blast Furnace Iron and Standard Steel Sample	40
5.2 Stepwise change in the Melt Temperature at Constant Manganese Addition to the Melt.	41
5.3 Stepwise Addition of Manganese at Constant Temperature.	41
5.4 Cooling of Melt at Different Cooling Rates	41
5.5 Effect of Lime Additions on Mn-S Interactions	44
5.6 Preparation of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag in mullite crucible.	44

CHAPTER VI	DISCUSSION	49
CHAPTER VII	SUMMARY AND CONCLUSIONS	58
CHAPTER IX	SUGGESTIONS FOR FURTHER WORK	60
REFERENCES		61

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>page</u>
2.1	Effects of Small Concentrations of Added Substances on Activity Coefficient of Sulphur.	11
2.2	Comparison of Values of f_s Obtained by Morris with the Calculated Values using Data of Sherman and Chipman.	14
5.1	Details of Experiment and Results of Stepwise Changes in the Melt Temperature at Constant Manganese Addition to the Melt.	22
5.2	Details of Experiment and Results of Stepwise Addition of Manganese at Constant Temperature.	33
5.3	Details of Experiment and Results of Cooling of Melt at Different Cooling Rates.	43
5.4	Details of Experiment and Results of Effect of Lime Additions on Mn-S Interactions.	47
6.1	Values of $[\%Mn] \times [\%S]$	50

LIST OF FIGURES

(vi)

<u>Figure No.</u>	<u>Title</u>	<u>page</u>
2.1	Effect of Sulphur Concentration on $K'_{2.1}$	7
2.2	Effect of Carbon Content on Activity Coefficient of Sulphur in Iron at 1600°C.	9
2.3	Effect of Alloying Elements on the Activity Coefficient of Sulphur in Iron at 1600°C.	12
2.4	Effect of Basicity on Desulphurisation at 1500°C.	15
2.5	Metal Iso-sulphur Lines for 1.5% Sulphur Slags at 1500°C and 1425°C.	17
2.6	Comparison of Laboratory Measurements of Sulphur Slag-Metal Partition with that Calculated from Thermodynamic Data.	19
2.7	Plot of $\log C_s$ against $N_{CaO} + 0.1 N_{MgO} - 0.8 N_{Al_2O_3} - N_{SiO_2}$ at 1575, 1600 and 1655°C.	20
4.1	Schematic Diagram of Silicon Carbide Furnace	23
4.2	Schematic Circuit Diagram for the Power Supply to the Silicon Carbide Furnace	30
4.3	Gas Train	32
4.4	Schematic Set-up for Sulphur Analysis	33
5.1	Variation of Temperature with Time for Different Cooling Rates in Heats No.7 and 8.	45
6.1	Variation of Sulphur Content of Melt with Temperature.	50
6.2	Effect of Manganese on Sulphur Content of Metal at 1400°C.	52
6.3	Variation of $\log [\%S]$ with $\log [\%Mn]$	53
6.4	Effect of Cooling on Sulphur Content of the Metal.	55

ABSTRACT

Many studies have been done in the last few decades to control the sulphur content in steel for its improved mechanical properties. Few studies are available in the temperature range of 1200-1400°C, the usual temperature found during the transit of blast furnace metal from the blast furnace to the mixer. In the present work, the effect of manganese on desulphurization of blast furnace metal in the temperature range of 1200-1400°C was studied. The experiments included the equilibrium studies on the Mn-S interactions in the metal through stepwise temperature changes and stepwise manganese additions, effect of cooling rate on the sulphur level of the melt and the effect of manganese on the desulphurizing power of lime. The viability of use of mullite crucible for slag-metal studies was also investigated. It was found that sulphur level in the melt decreases with decrease in temperature. The solubility product of manganese and sulphur remains constant at a given temperature, confirming the theoretical prediction and findings of other investigators. Cooling leads to an immediate lowering of sulphur content, independent of the cooling rate. The effect of 10% addition of lime resulted in around 20% lowering of sulphur content of metal. Manganese addition alongwith lime enhanced the extent of desulphurisation with the formation of manganese sulphide. It was found that the mullite crucible cannot be used for the prolong slag-metal equilibrium studies at 1400°C.

CHAPTER I

INTRODUCTION

1.1 Importance of Sulphur Control in Steel

Low sulphur in steel is essential for improved mechanical properties such as ductility, impact resistance, cold pressing properties and to avoid cracking failure as well as directional anisotropy in mechanical properties on hot working. For general applications steel may have 0.025 to 0.040 percent sulphur while for special steel, it must be below 0.01 percent. Free cutting steel is the only grade of steel where the sulphur content is deliberately kept high viz. 0.22 weight percent or more. Thus it is essential that strict control of sulphur in steel be maintained.

1.2 Origin of Sulphur in Steel

The major source of sulphur in steel is the coke used in blast furnace. A small fraction also enters with sinter or iron ore. In the blast furnace, as the coke burns at the tuyeres, sulphur is picked up by the H_2 and CO gases to form H_2S and COS. As these gases come in contact with iron bearing and CaO bearing materials, sulphur is absorbed to form FeS and CaS and it descends back to the lower part alongwith the rest of the materials in the molten form. Further transfer of sulphur from metal to the slag or vice versa occurs in the hearth.

1.3 Control of Sulphur in Steel

The main control of sulphur is done in the blast furnace stage itself, the extent of sulphur removal during steel-making being small. It is estimated that 80-90% of the sulphur input is removed in the slag in the blast furnace while the rest goes in the metal. The factors that control the sulphur content in blast furnace include the coke rate, sulphur content of coke, slag volume and the sulphur distribution ratio α i.e. (% S in slag)/(% S in hot metal). Mathematically sulphur balance gives the following :

$$[\text{wt.}\% \text{S}] = \frac{(\text{wt.}\% \text{S})_{\text{coke}} \times \text{coke rate}}{1000 + \alpha \times W_{\text{sl}}}$$

where $[\text{wt.}\% \text{S}]$ is the percentage of sulphur in hot metal and W_{sl} is the amount of slag produced per tonne of hot metal. Since slag rate should be kept low for other advantages and coke rate cannot be changed appreciably low sulphur can be achieved only at high sulphur distribution ratios. High sulphur distribution ratios can be obtained by maintaining high slag basicity high metal temperature and low FeO level in the slag. Removal of sulphur during steelmaking is limited due to high FeO content in the slag. It is not possible to have sulphur distribution ratios greater than 5 or 10 and in most cases only fifty percent of sulphur can be removed from the melt during refining.

1.4 External Desulphurisation

Techno-economic considerations do not justify sulphur removal to low levels either in blast furnace or in LD steel making. So resort is being made to a much greater extent nowadays to external desulphurisation. Desulphurizing agents such as soda ash, lime calcium carbide or magnesium are either added or injected to the metal in a suitable manner to enhance the rate of sulphur removal from the metal to the slag. Various methods have been used for external desulphurisation during the last two decades and the same have been summarised by many investigators.

1.5 Scope of the Present Investigation

There have been many basic and applied studies in the last 20-30 years to show the effects of various additions on the degree of desulphurisation of iron. It is now known that the presence of carbon and silicon in metal helps in sulphur removal by increasing its activity coefficient. The effects of various elements on the solubility and activity of sulphur in the liquid iron are now well known. For example, solubility of sulphur is known to be lowered by presence of manganese in metal and this has been exploited in some plants including the Rourkela Steel Plant in India. The Fe-C-Mn system has been scientifically investigated by Pattjoshi⁽¹⁾ in the temperature range 1200-1400°C. The present work involved the studies on the manganese-sulphur interactions in the blast furnace metal obtained from Rourkela Steel Plant. Attempts were made to simulate the metal in the ladle as to show the

extent of sulphur removal during transfer of metal from blast furnace to the mixer stage in the plant. The work involved designing and setting up of suitable arrangements in the laboratory for studying the reactions under controlled conditions.

CHAPTER II

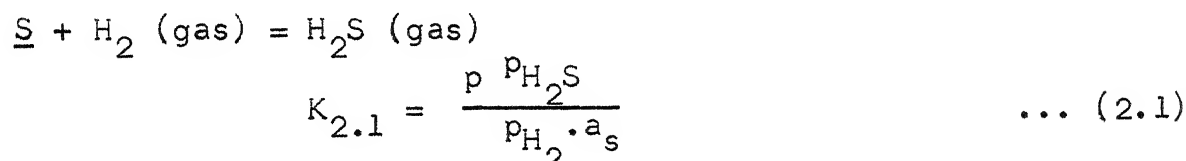
LITERATURE SURVEY

Much work has been done in the past few decades regarding the activity of sulphur in liquid iron and steel, sulphur partition between slag and metal in the blast furnace and sulphide capacity of various slags. An attempt is being made here to review briefly the work done in the past in this field.

2.1. Activity of Sulphur in Liquid Iron Alloys

2.1.1 General approach to activity determination

The experiments designed to study sulphur activity were based on the attainment of equilibrium between sulphur in the melt and gaseous atmospheres containing hydrogen and hydrogen sulphide. The reaction is :



where $p_{\text{H}_2\text{S}}$ and p_{H_2} are the partial pressures of H_2S and H_2 respectively in the gas mixture and a_s represents the activity of sulphur in the metal, being given by

$$a_s = f_s [\text{wt.}\% \text{S}]$$

where f_s is the activity coefficient of sulphur in the liquid metal and $[\text{wt.}\% \text{S}]$ is the percentage of sulphur in the melt.

In a multicomponent system containing solutes 1,2,3,4... f_s is given by the following equation :

$$\log f_s = \log f_{Si} + \log f_{Si} + \dots$$

where $\log f_{Si} = e_s^i [\text{wt.}\% i)$... (2.2)

e_s^i being the Henrian interaction parameter in one weight percent standard state. It gives the effect of the solute 'i' on the activity coefficient and is defined as :

$$e_s^i = \left(\frac{\partial \log f_s}{\partial [\text{wt.}\% i]} \right)_{\text{wt.}\% j, k \dots \dots 0}$$

As the concentrations of all solutes tend to zero, f_s tends to one and $K'_{2.1}$ is then given by

$$K'_{2.1} = \frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{[\text{wt.}\%]S} \dots (2.3)$$

At any other concentration of sulphur $K'_{2.1}$ can be found by fixing p_{H_2S}/p_{H_2} ratios and finding the corresponding $[\text{wt.}\%S]$ in the melt. A typical plot of $\log K'_{2.1}$ versus sulphur percent is shown in Fig. 2.1. $K_{2.1}$ is determined from the intercept of the line at zero concentration. And for any finite concentration activity coefficient of sulphur can be defined as follows

$$f_s = \frac{K'_{2.1}}{K_{2.1}} \dots (2.4)$$

2.1.2 Fe-S system

Banya and Chipman⁽²⁾ calculated the standard free energy of formation of H_2S from the gases H_2 and S_2 and reported it as follows :

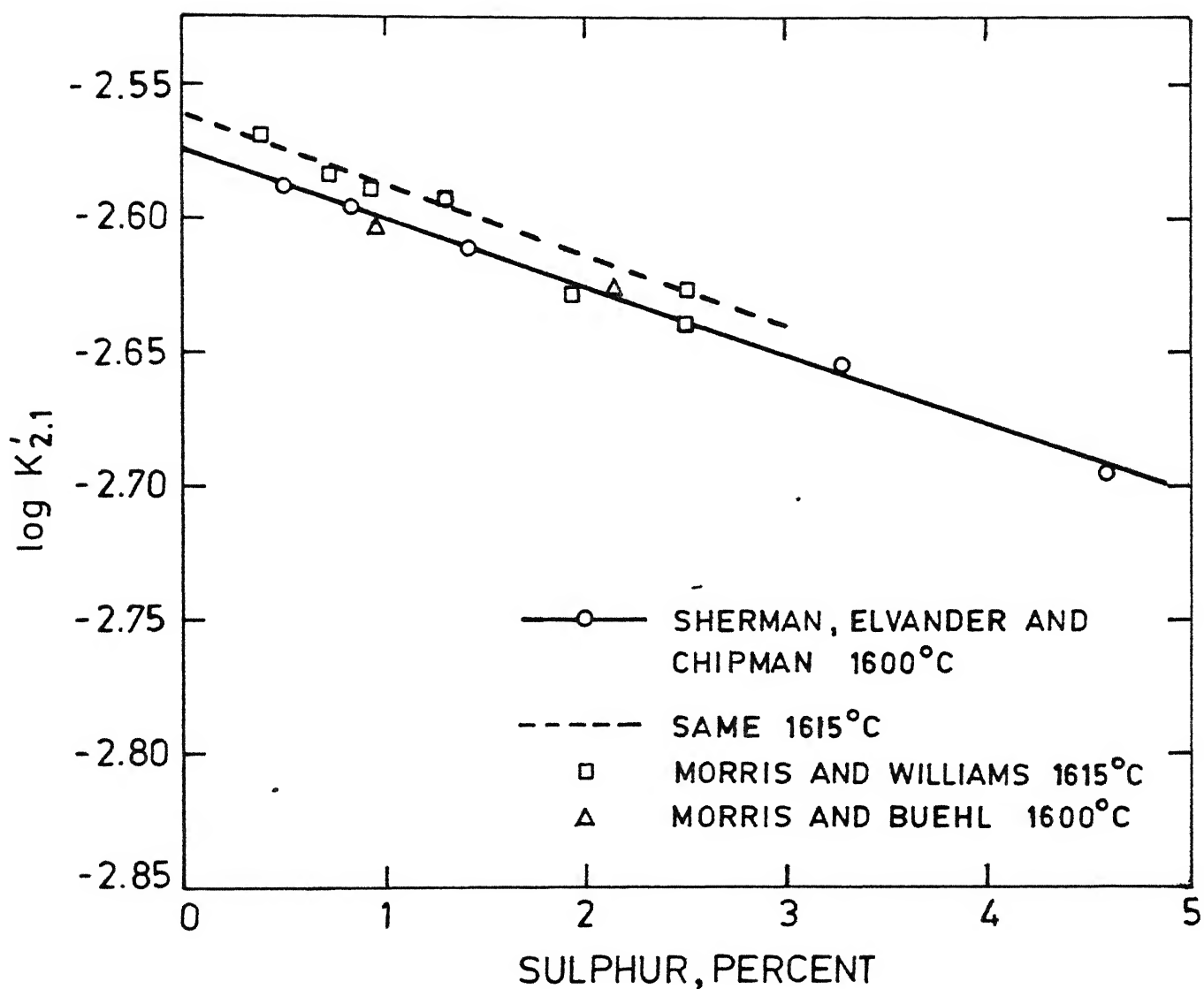
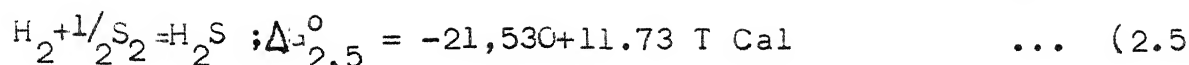
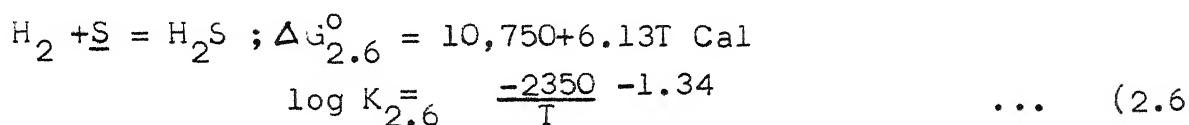


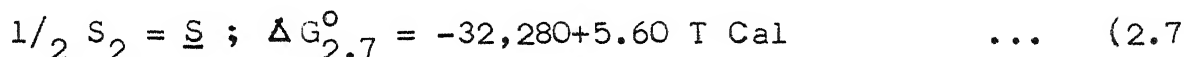
FIG. 2.1 EFFECT OF SULPHUR CONCENTRATION ON $K'_{2.1}$.
(Ref. 6, 18 and 19).



They also determined the equilibrium constant experimentally as a function of temperature in the range of 1500-1600°C and for calculation purposes they took into account the dissociation of H_2S into HS , S_2 and $\text{S}(\text{gas})$. They reported the following results :



Combining equations 2.5 and 2.6 we have,



Thus they gave the following variation of f_s with sulphur content which was valid upto 3 percent sulphur :

$$\log f_s = -0.0282 [\%S]$$

The value e_s^S of -0.0282 agrees with the value used by investigators earlier.⁽³⁾

2.1.3 Ternary systems

Morris and Beuhl⁽⁴⁾ studied the effect of carbon on the activity of sulphur in liquid iron by equilibrating the melt with H_2 - H_2S gas mixtures. Their results are shown in Fig. 2.2. They showed that carbon has a definite influence on the activity of sulphur in dilute solutions of sulphur in liquid iron. It was also seen that the activity of sulphur dissolved in liquid iron-carbon alloys increases with a rise in temperature. However, the temperature effect was small except at carbon saturation, where a rise in temperature was accompanied with a rise in sulphur activity resulting from the carbon increase.

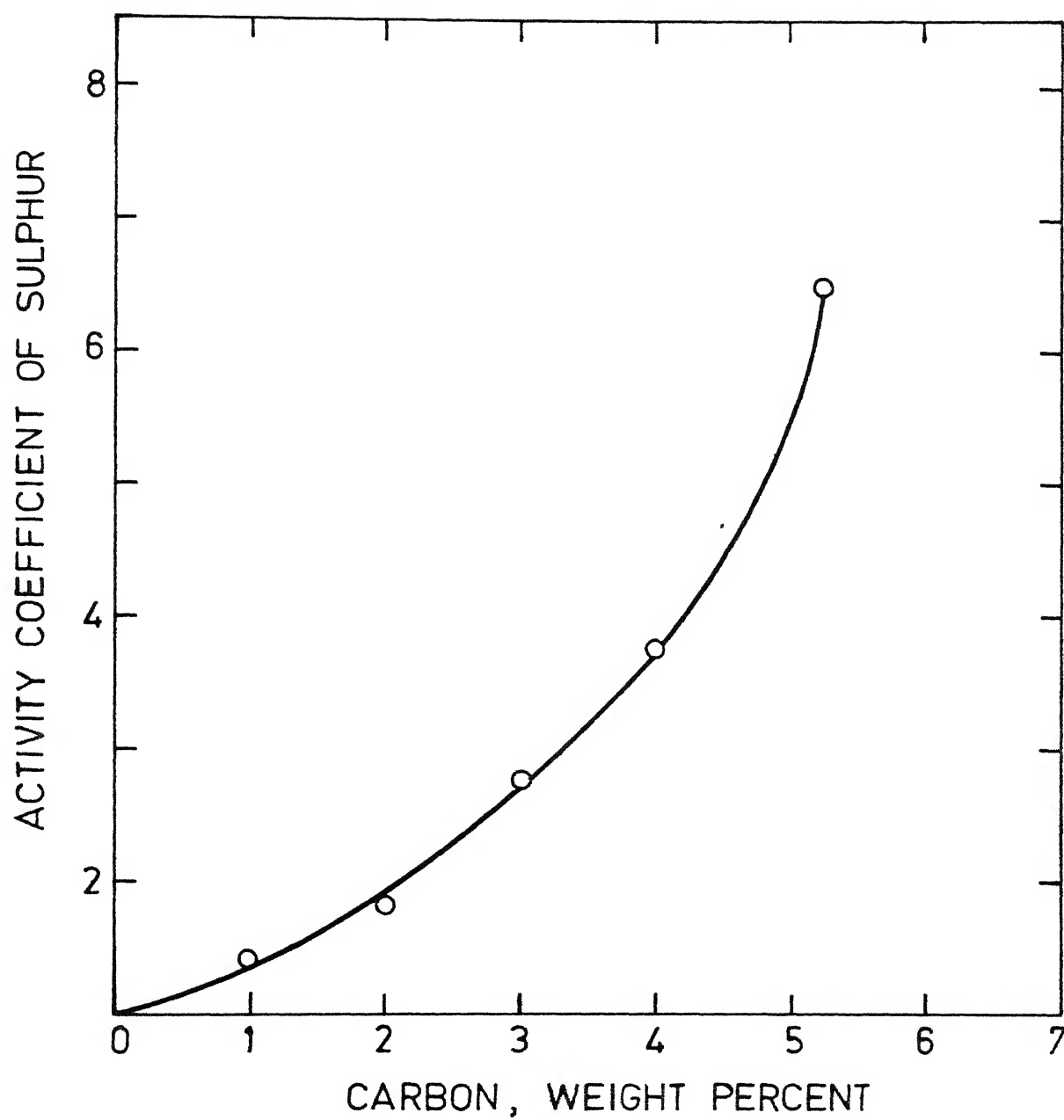


FIG. 2.2 EFFECT OF CARBON CONTENT ON ACTIVITY COEFFICIENT OF SULPHUR IN IRON AT 1600°C. (Ref. 6)

From Fig. 2.2, e_s^C could be 0.12 upto carbon concentrations of 1 or 2 wt. percent, but for carbon concentration beyond 2 percent, $\log f_s$ versus [wt.%C] plot is not linear and equation 2.2 cannot be applied directly to find e_s^C values. The slope of $\log f_s$ versus [%C] plot at 4-5 pct. carbon level is around 0.24 which has been reported as the interaction parameter value by some investigators later.⁽⁵⁾ Morris and Beuhl used 4.35 percent carbon in iron as its standard state and reported the following :

$$\frac{1}{2} S_2(g) = \underline{S}(4.35\%C) ; \Delta G_{2.8}^0 = -23,880 + 3.90 T \text{ cal} \dots (2.8)$$

Equation 2.8 is related to equation 2.7 by the following :

$$G_{(4.55\%C)}^0 = \Delta G^0 + RT \ln f_s^C$$

f_s^C is found to be 4.2 at 1600°C and 4.35 percent carbon. Since the slope of $\log f_s$ versus [%C] plot is 0.24 at this carbon level, f_s^C at any other level of carbon can be determined as follows :

$$\log f_s^C = \log 4.2 + 0.24 (x-4.35) \dots (2.9)$$

where x is the weight percent of carbon in the melt.

Sherman and Chipman⁽³⁾ studied various ternary systems in relation to the activity of sulphur. They plotted $\log f_s$ versus [wt.%i] in many cases including manganese, phosphorous, aluminium, copper and carbon. From the curve e_s^i can be calculated in each case using equation 2.2. Their results are summarised in Table 2.1, and Fig. 2.3. They also suggested a semi-empirical method for calculating the activity coefficient

Table 2.1 (Ref. 3)

Effects of Small Concentrations of Added Substance
on Activity Coefficient of Sulphur.

i = third component	e_s^i
C	+ 0.113
Si	+ 0.065
P	+ 0.043
Al	+ 0.054
Cu	- 0.013
Mn	- 0.025

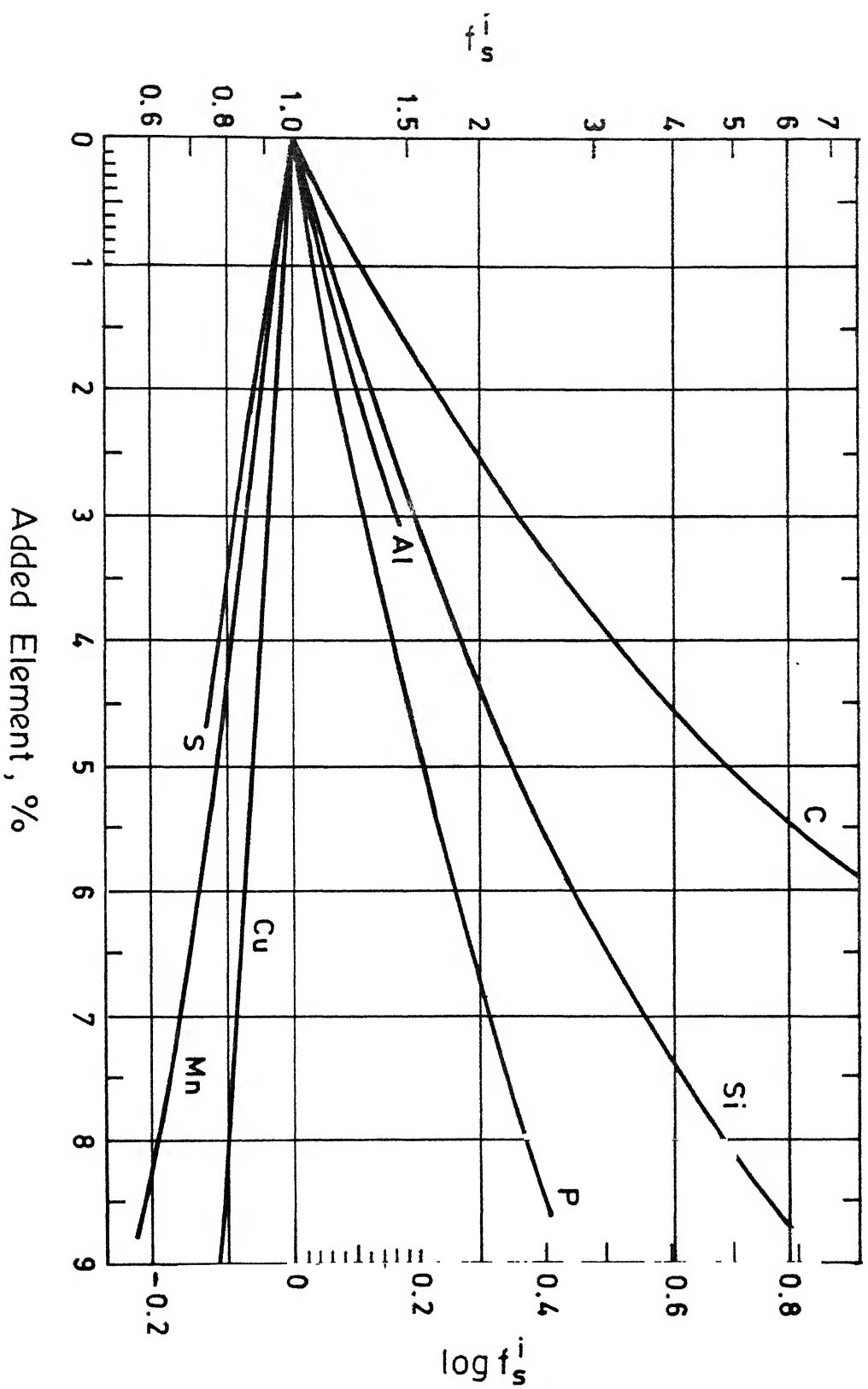


FIG. 2.3 EFFECT OF ALLOYING ELEMENTS ON ACTIVITY COEFFICIENT OF SULPHUR IN IRON AT 1600°C. (Ref. 3)

of sulphur in complex solution of four or more components. This method was tested by them against extensive data on solutions of this kind and found to be reasonably accurate.

Morris⁽⁶⁾ investigated the effect of manganese on the activity of sulphur in liquid iron and iron-carbon alloys. His results are given in Table 2.2. His experimental results match well with those of Sherman and Chipman⁽³⁾ as can be seen by the good agreement in f_s values in Table 2.2.

Pattjoshi⁽¹⁾ in his work on Mn-S interactions in iron-carbon alloys found consistent lower values of sulphur at 1300°C and 1400°C compared with the theoretical values. This was attributed to the higher activity coefficient of sulphur in the melt than reported in literature or error in estimation of the standard free energy of the reaction.

2.2 Slag-Metal Equilibrium

Hatch and Chipman⁽⁷⁾ studied the sulphur distribution equilibria between the blast furnace slag and metal. They found that the best correlation between desulphurization ratio and basicity was obtained when the latter was expressed as

$$\frac{\text{CaO} + 2/3 \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \quad (\text{in molar terms})$$

suggesting that magnesia was not as effective as lime as a desulphurizing agent. (Fig. 2.4). A better correlation was obtained with excess base expressed as $(\text{CaO} + 2/3 \text{MgO}) - (\text{Al}_2\text{O}_3 + \text{SiO}_2)$ (in moles per 100 gm of slag). From studies at two different

Table 2.2 (Ref. 14)

Comparison of Values of f_s Obtained by Morris
with the Calculated Values using Data of Sherman
and Chipman.

Temp (°C)	$\frac{H_2S}{H_2} \times 10^3$	C (%)	Mn (%)	S (%)	f_s (Morris)	$f_s = f_s^c f_s^S f_s^{Mn}$ (calculated)
1600	2.36	0.0	2.2	1.04	0.90	0.83
1600	2.40	2.2	1.8	0.54	1.77	1.47
1600	2.42	4.0	2.8	0.29	3.32	2.63
1600	2.37	Saturated	2.8	0.17	5.55	5.46
1500	2.40	Saturated	2.4	0.19	5.84*	-
1400	2.34	Saturated	1.0	0.20	6.50*	-

*Recalculated by using equation (2.6) and Morris's data.

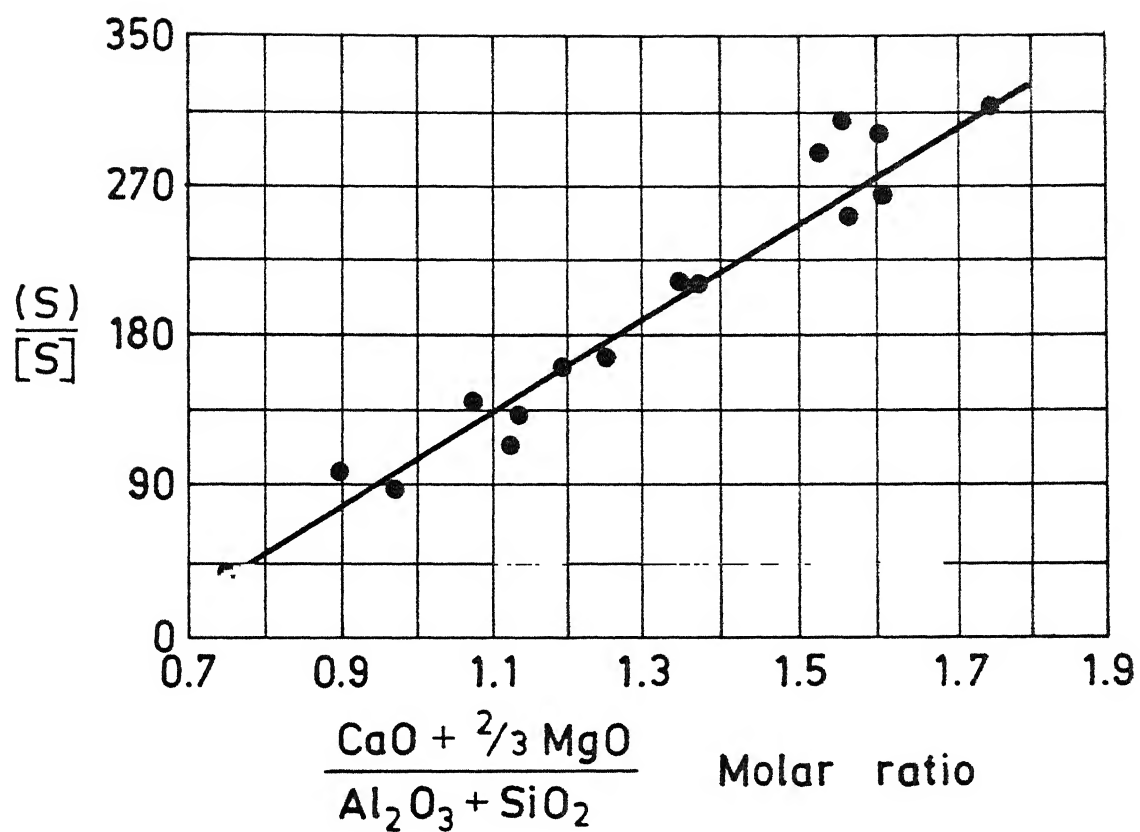
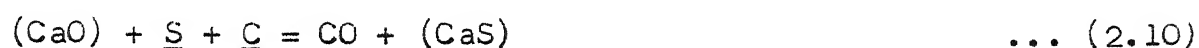


Fig. 2.4. Effect of basicity on desulphurization at 1500 °C (Ref. 7).

temperatures of 1500°C and 1425°C they plotted on a ternary diagram isosulphur lines (Fig. 2.5). The diagram summarizes the effect of slag composition and temperature in the equilibrium sulphur concentrations in liquid pig iron.

Venkatdri and Bell⁽⁸⁾ tried to express sulphur partition between slag and metal in the blast furnace in terms of sulphide capacity of slags. Sulphur equilibrium between slag and metal was expressed as :



Activities of CaO, CaS are not accurately known, but there is much data on sulphide capacities of these slags, the capacity C_s being given by :

$$C_s = (\text{wt.}\% \text{S}) \frac{\text{PO}_2^{1/2}}{\text{PS}_2^{1/2}}$$

Kalyanram et al⁽⁹⁾ have measured sulphide capacities over a wide range of slag compositions and had found a correlation with an empirical basicity ratio $\frac{N_{\text{CaO}} + 1/2 N_{\text{MgO}}}{N_{\text{SiO}_2} + 1/3 N_{\text{Al}_2\text{O}_3}}$ where N denotes mole fraction. Their results have been re-examined by

Venkatdri and Bell and may be summarized as follows :

$$\log C_s = -5.57 + 1.39 \frac{N_{\text{CaO}} + 1/2 N_{\text{MgO}}}{N_{\text{SiO}_2} + 1/3 N_{\text{Al}_2\text{O}_3}}$$

$$+ 1.58 \times 10^{-3} [T(^{\circ}\text{C}) - 1500]$$

Using thermodynamic data for sulphur solution and CO formation, they expressed sulphur partition as :

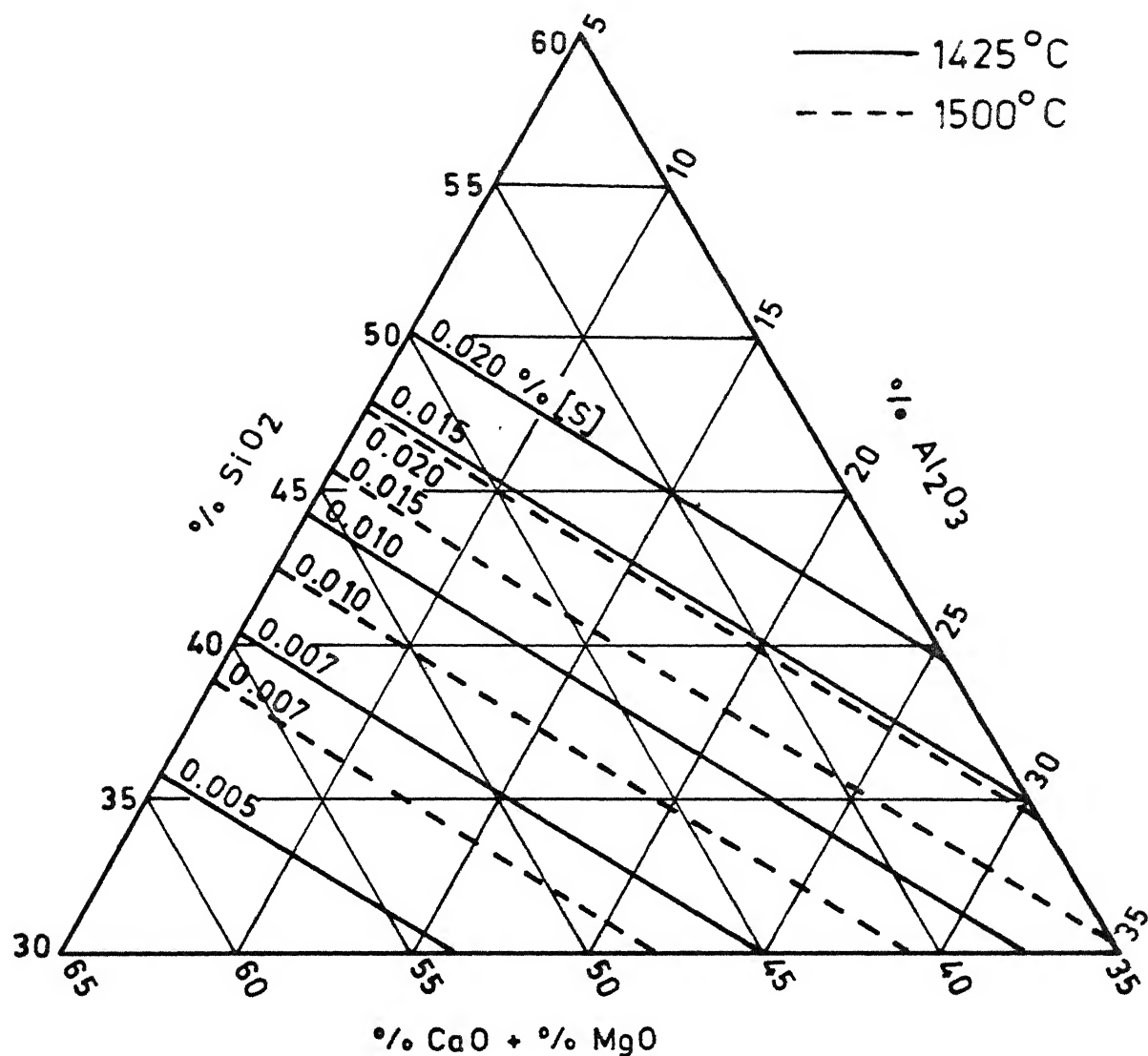


FIG. 2.5. METAL ISO-SULPHUR LINES FOR 1.5 % SULPHUR SLAGS AT 1500°C AND 1425°C. (SLAG. COMPOSITION IN WEIGHT %). (Ref. 7)

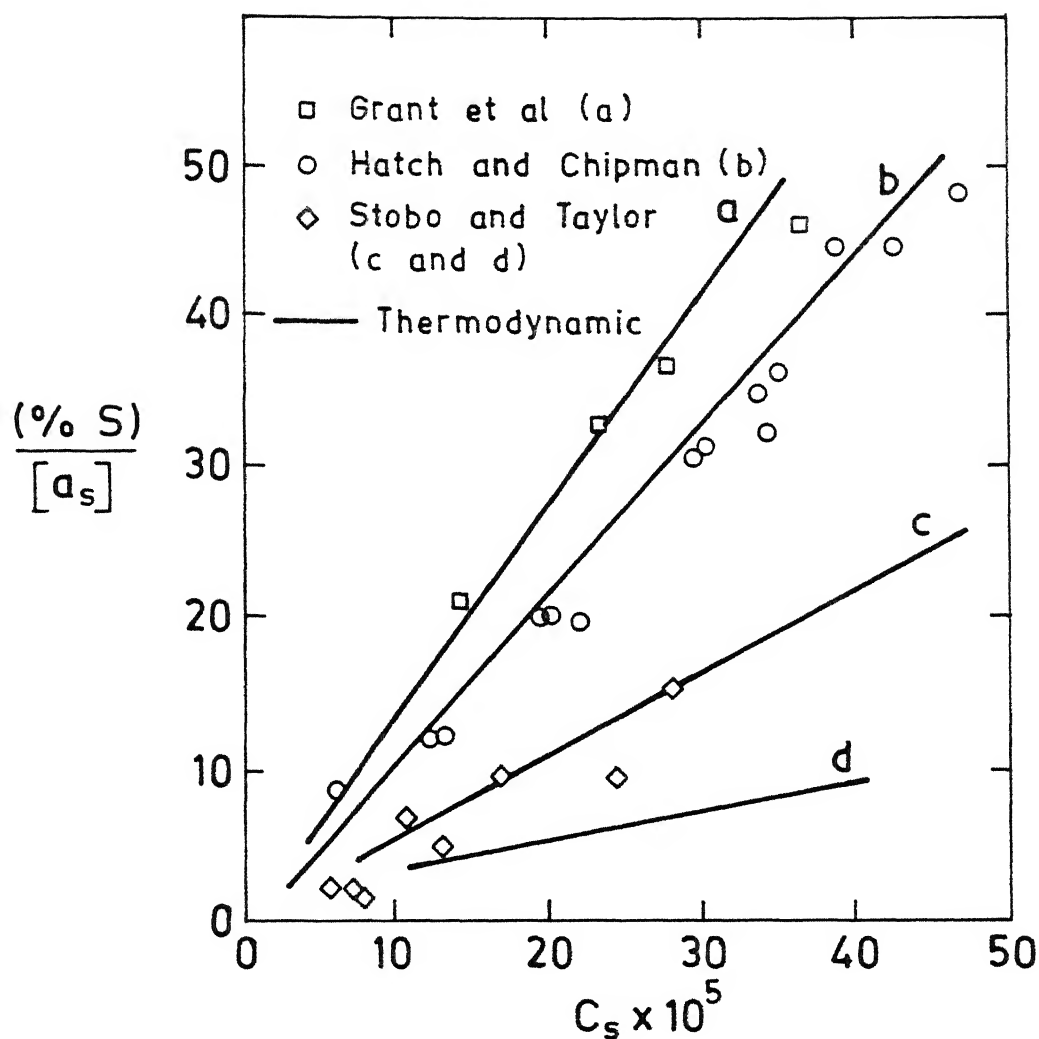


Fig. 2.5. Comparison of laboratory measurements of sulphur slag metal partition with that calculated from thermodynamic data (Ref. 8).

- a : a_c 1; $P_{CO} = 1 \text{ atm}$, $T = 1525^\circ \text{C}$
 b : a_c 1; $\text{FeO} = 0.05\%$, $T = 1500^\circ \text{C}$
 c : a_c 1; $\text{FeO} = 0.1\%$, $T = 1500^\circ \text{C}$
 d : a_c 1; $\text{FeO} = 0.2\%$, $T = 1500^\circ \text{C}$

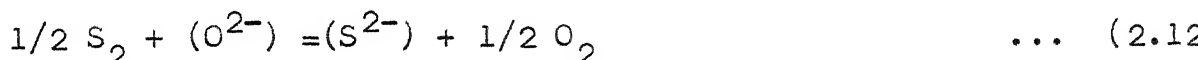
$$\log \frac{(\%S)}{[a_S]} = (5.55 - \frac{724}{T}) + \log C_S + \log a_c/PCO \quad \dots (2.1)$$

In terms of ferrous oxide content of slag :

$$\log \frac{(\%S)}{[a_S]} = (\frac{5543}{T} - 1.43) + \log C_S + \log \frac{a_{Fe}}{a_{FeO}}$$

Their results are shown in Fig. 2.6.

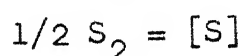
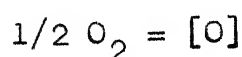
Tsao and Katayama⁽¹⁰⁾ measured the equilibrium sulphur distribution between liquid iron and CaO-MgO-Al₂O₃-SiO₂ slag of calcium aluminate base in the temperature range 1575 to 1650°C and derived experimental equations for sulphide capacity. They used the following equation for definition of sulphide capacity :



$$\begin{aligned} C_S &= (\text{wt.}\%S) \cdot (PO_2)^{1/2}/(PS_2)^{1/2} \\ &= K_{2.12} a_o^{2-}/f_s^{2-} \quad \dots (2.13) \end{aligned}$$

where $K_{2.12}$ is the equilibrium constant for reaction 2.12.

Using equilibrium constant for reactions



they calculated the sulphide capacity as :

$$\begin{aligned} \log C_S &= 3.44 [N_{CaO} + 0.1 N_{MgO} - 0.8 N_{Al_2O_3} - N_{SiO_2}] \\ &\quad - \frac{9894}{T} + 2.05 \end{aligned}$$

(Fig. 2.7)

And thus they calculated the partition ratio as,

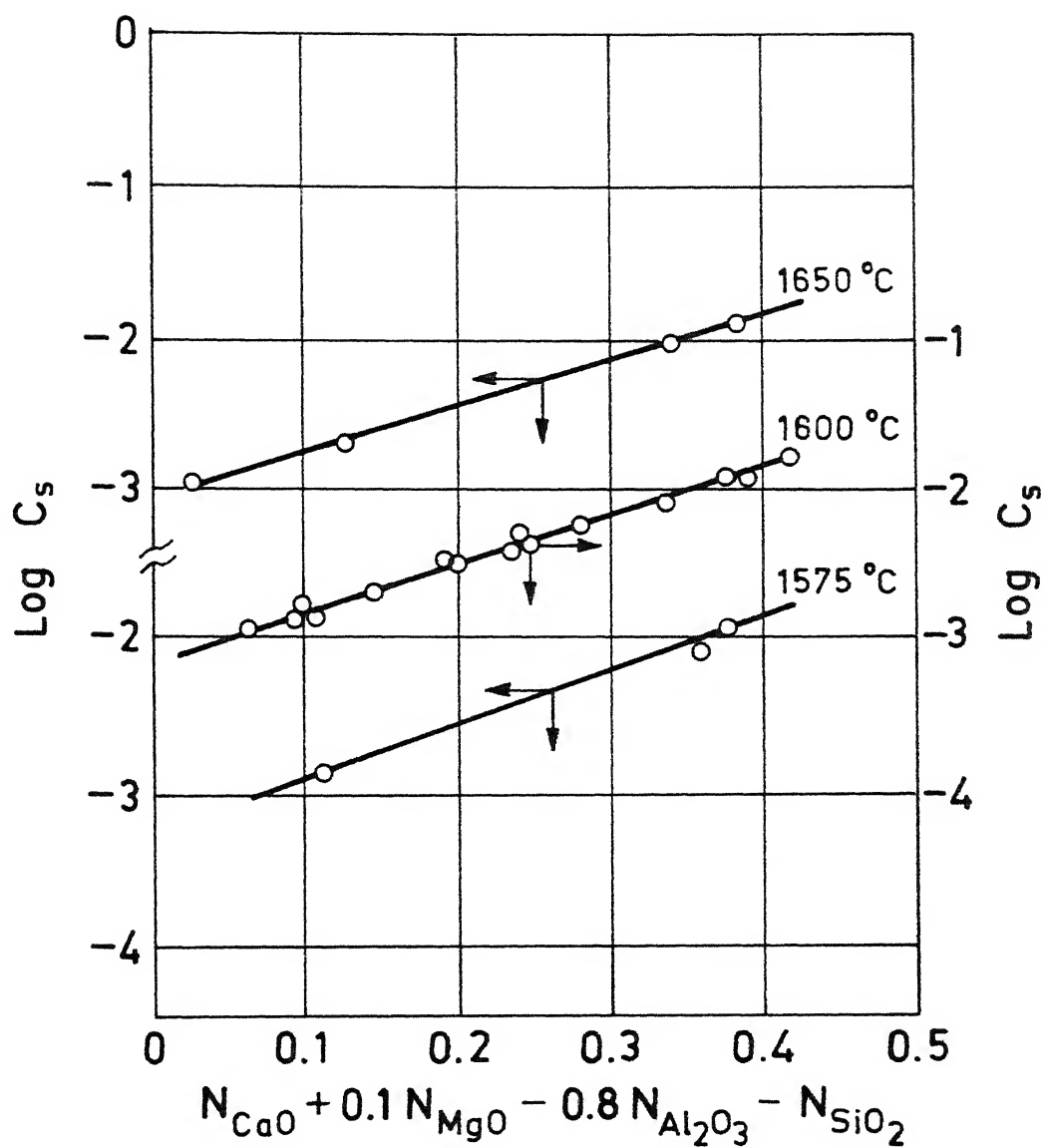


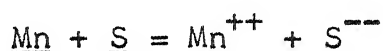
Fig. 2.7. Plot of the $\log C_s$ against $N_{CaO} + 0.1 N_{MgO} - 0.8 N_{Al_2O_3} - N_{SiO_2}$ at 1575, 1600 and 1650 °C (Ref. 9).

$$\log \frac{(\text{wt.}\%S)}{[\text{wt.}\%S]} = 3.44 (N_{\text{CaO}} + 0.1 N_{\text{MgO}} - 0.8 N_{\text{Al}_2\text{O}_3} - N_{\text{SiO}_2})$$

$$- \log [\text{wt.}\%O] - 10,980/T + 3.50 \quad \dots \quad (2.14)$$

2.3 Departure from Equilibrium in Blast Furnace

Filer and Carken⁽¹¹⁾ tried to study the extent of the departure from equilibrium with respect to sulphur distribution in the blast furnace by remelting blast furnace metal and slag under laboratory conditions. They found that the metal and slag in the blast furnace were not at equilibrium in regards to sulphur. On remelting, sulphur attained equilibrium, much faster than the manganese and silicon. They also found evidences of manganese-sulphur coupled reaction i.e.

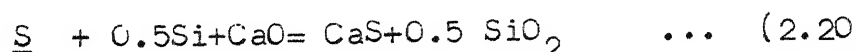
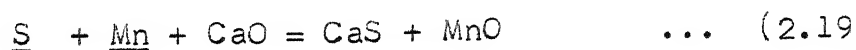
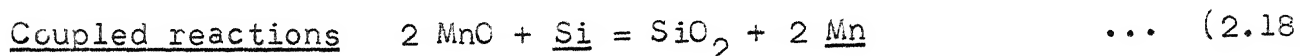


reaching equilibrium. The conclusions derived by them may not be valid since in a blast furnace partial pressure of CO gas in the hearth at the slag-metal interface will be much greater than 1.0 atm. which they have assumed.

Turkgodan et al⁽¹²⁾ studied blast furnace equilibrium in terms of partial equilibria. Two types of overall reactions : (a) primary reactions and (b) coupled reactions could be considered i.e.



These primary reactions involve volatile reaction products which impede the ultimate approach to equilibrium because of continuous loss of material from the system. So coupled reactions not involving volatile products were considered.



They found that although the system as a whole may not be at equilibrium with respect to the primary reactions, a state of partial equilibrium can exist between metal and slag with respect to one or more of the coupled reactions. They found equilibrium constant as a function of basicity B defined as

$\frac{\% \text{CaO} + \% \text{MgO}}{\% \text{SiO}_2}$ from the plant data as follows :

$$\log K_{2.18} = \log \frac{[\% \text{Mn}]}{(\% \text{MnO})}^2 \cdot \frac{(\% \text{SiO}_2)}{[\% \text{Si}]^2} = 2.8 B - 1.16$$

$$\log K_{2.19} = \log \frac{(\% \text{S})}{[\% \text{S}]} \cdot \frac{(\% \text{MnO})}{[\% \text{Mn}]} \cdot \frac{1}{(\% \text{CaO})} = \frac{6327}{T} - 3.85$$

$$\log K_{2.20} = \log \frac{(\% \text{S})}{[\% \text{S}]} \cdot \frac{(\% \text{SiO}_2)^{1/2}}{[\% \text{Si}]} \cdot \frac{1}{(\% \text{CaO})} = \frac{6327}{T} - 4.43 + 1.413$$

The above conclusions may have to be modified if the actual P_{CO} in the blast furnace is greater than one. Biswas⁽¹³⁾ reported a better agreement between the plant data and the theoretical calculation based on laboratory data if P_{CO} is assumed to be around 2.5 atm. rather than 1.0.

2.4 Effect of Manganese on Desulphurisation

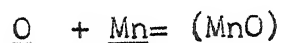
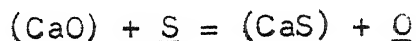
Grant et al⁽¹⁴⁾ studied the effect of Mn and MnO when added to initial charge or during the course of a heat. Addition of MnO led to an immediate and temporary reversion of sulphur into the metal. This was ascribed to the increase in oxygen potential of slag, an effect similar to FeO addition. With reduction of MnO, the reversal ceased. Effect of manganese on both desulphurisation rate and equilibrium was very small and confined to the less basic slags. And they found that increase in manganese the melt appeared to parallel the course of desulphurisation.

In another study Grant et al⁽¹⁵⁾, tried to represent manganese level in the metal as an indicator of desulphurisation. They found that manganese reduction was a better indicator of desulphurisation than any common measure of slag basicity. They also confirmed the reversion of sulphur from slag to metal due to additions of oxygen to the system (derived from MnO or Fe_3O_4).

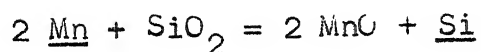
Frohberg et al⁽¹⁶⁾ studied the kinetics of sulphur transfer between iron melts and metallurgical slags. They found that an increase in manganese content of metal caused an increase in the sulphur transfer rate.

Pattjoshi⁽¹⁾ showed that with increased manganese level in the melt, the sulphur gets transferred in the lime based slags to a greater degree. Following reasons were attributed to this :

- (1) Formation of MnS : The activity of MnS in the slag is lowered due to the presence of liquid lime based slag.
- (2) Manganese enhances the rate of sulphur removal by CaO in the slag as per the following reactions :



- (3) Manganese in melt reacts with SiO_2 in slag to form silicon in the melt and MnO in slag as per reaction :



This increases the basicity of the slag lending to lower sulphur level in the metal. He suggested that all the three factors listed above might be responsible for the lowering of sulphur level in presence of manganese in the melt.

CHAPTER III

PLAN FOR PRESENT WORK

Few scientific studies have been done on manganese-sulphur reactions in the temperature range of 1200-1400°C, which is the usual temperature occurring during the transit of metal from the blast furnace to the mixer and during external desulphurisation of iron. Pattjoshi⁽¹⁾ tried to study the system by taking almost pure iron carbon saturated alloys in this temperature range. In the present work, the work was extended to the blast furnace iron itself. The work basically consisted of the following :

- (1) Setting up the experimental arrangement for studying iron-carbon system in the temperature range of 1200-1400°C. It included repairing a silicon carbide furnace, melting the pig iron under argon atmosphere in a mullite crucible and drawing samples very carefully using quartz tube. For some experiments calcium oxide was prepared in the lab by calcining calcite. The samples were suitably crushed and analyzed for manganese and sulphur.
- (2) The experiments involved :
 - (i) Melting of pig iron at various temperature to record any changes in the sulphur content with temperature.
 - (ii) Adding one percent sulphur in the form of FeS and manganese metal additions to the alloy at 1400°C and to study the variation of sulphur with stepwise changes in temperature for cooling and heating.

- (iii) Stepwise addition of manganese upto 4% in the melt of pig iron and one percent sulphur at the temperature of 1400°C .
- (iv) Cooling of pig iron without stirring at two different rates as to simulate the transport of ladle from the blast furnace to the mixer.
- (v) Studying the effect of lime additions on desulphurisation at two different levels of manganese addition.
- (vi) Preparation of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slag in a mullite crucible and studying the viability of using such slags for future studies on slag-metal equilibrium using these crucibles.

CHAPTER IV

EXPERIMENTAL DETAILS

4.1 Equipments

4.1.1 Silicon carbide furnace

A silicon carbide furnace of outer diameter 40 cm. and length 50 cm. fabricated in the laboratory was basically the same as that used by Pattjoshi.⁽¹⁾

The inner part of the furnace schematically shown in fig. 4.1 is insulated by 10 cm. thick hot face insulation bricks in a cylindrical fashion, while the outer layer of insulation consists of 5 cm. thick, 85% MgO, 15% asbestos powder mix. The above is surrounded by a metal sheet while the bottom and top of the furnace are suitably insulated using 4 mm. thick asbestos sheets.

The furnace tube consisted of an aluminium tube 3.8 cm. i.d. and 60 cm. long with end closed and it rested on a refractory base at the bottom. The tube was filled with alumina powder upto the high temperature zone of the furnace. In some experiments, it was replaced by an open mullite tube of 5 cm. i.d., 60 cm. length, one end being closed using a refractory plug. Here refractory chips were used for filling upto the high temperature zone of the furnace.

4.1.2 Furnace circuit

The power to the furnace was supplied using a 40A, continuously adjustable single phase, oil cooled auto trans-

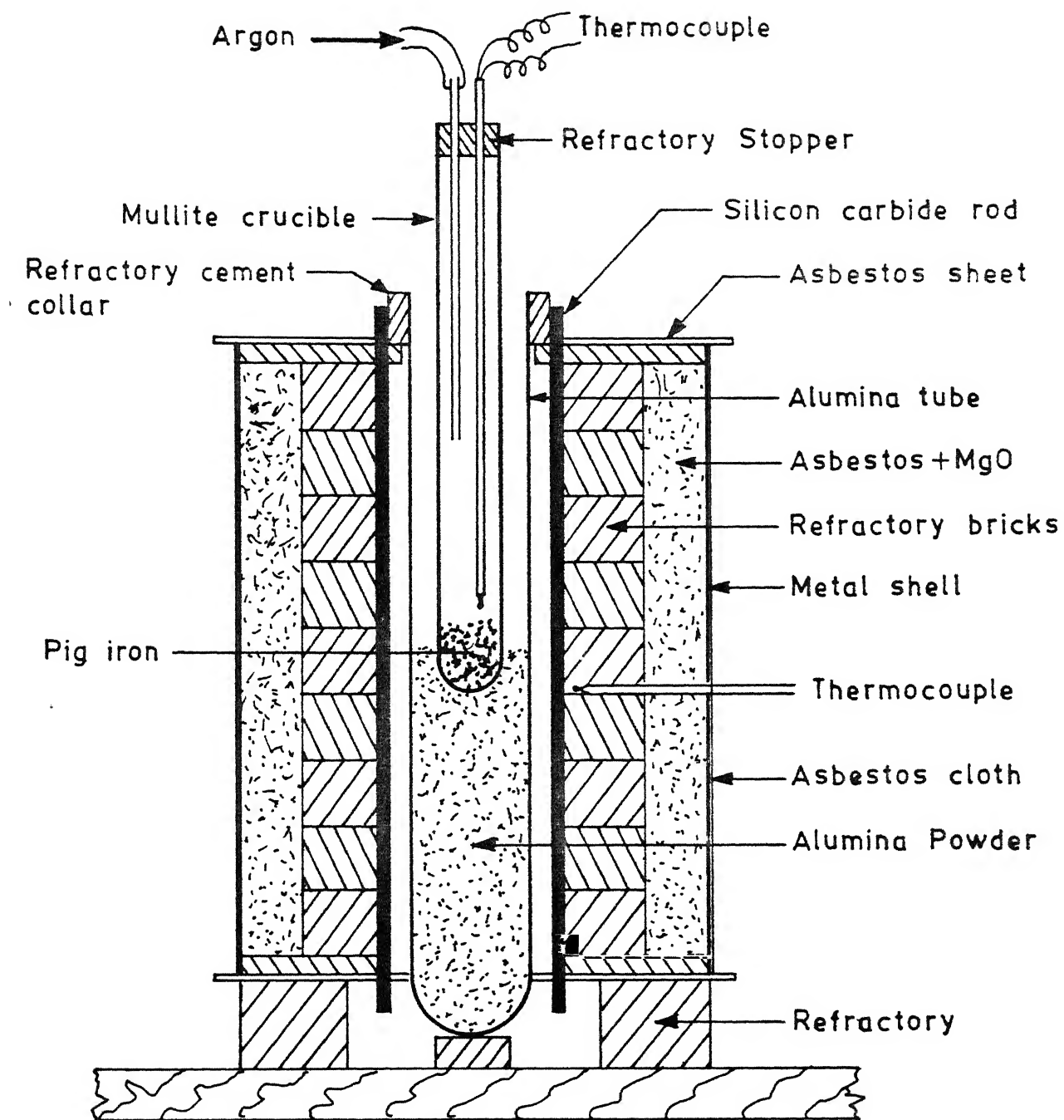


Fig. 4.1. Schematic Diagram of Silicon Carbide Furnace.

former with 220 volts input and 0-240 volts output. The schematic diagram of the circuit is shown in fig. 4.2.

The power from the mains to the transformer was supplied via an on-off temperature controller. A 2-3 ohms resistance silicon carbide furnace was connected in parallel to the controller relay in order to supply power to the furnace at a reduced rating when the controller was in off position. The uninterrupted supply of current to the heating elements leads to better temperature control and longer life of silicon carbide rods. These arrangements helped to control the temperature of the reaction tube in the furnace within the limits of $\pm 2^{\circ}\text{C}$.

4.1.3 Thermocouple

Platinum-Platinum + 10% Rhodium thermocouple of 0.5 mm. dia and 20 cm. length was used to control the furnace temperature. A separate 75 cm long platinum-platinum+10% Rhodium thermocouple of the same dia was used to measure the exact temperature of the melt. These thermocouples have been calibrated with melting point of pure copper and with a standard Platinum-Platinum+10% Rhodium thermocouple supplied by NPL, Delhi. The open ends of the 75 cm. long thermocouple were connected to the cold junction through compensating wires. The cold junction consisted of 5 mm. i.d. glass tubes containing mercury and immersed in ice kept in a thermos. The cold junction was connected to the millivolt digital potentiometer through copper lead wires. The e.m.f. showed by the potentiometer was converted to temperature using standard tables.

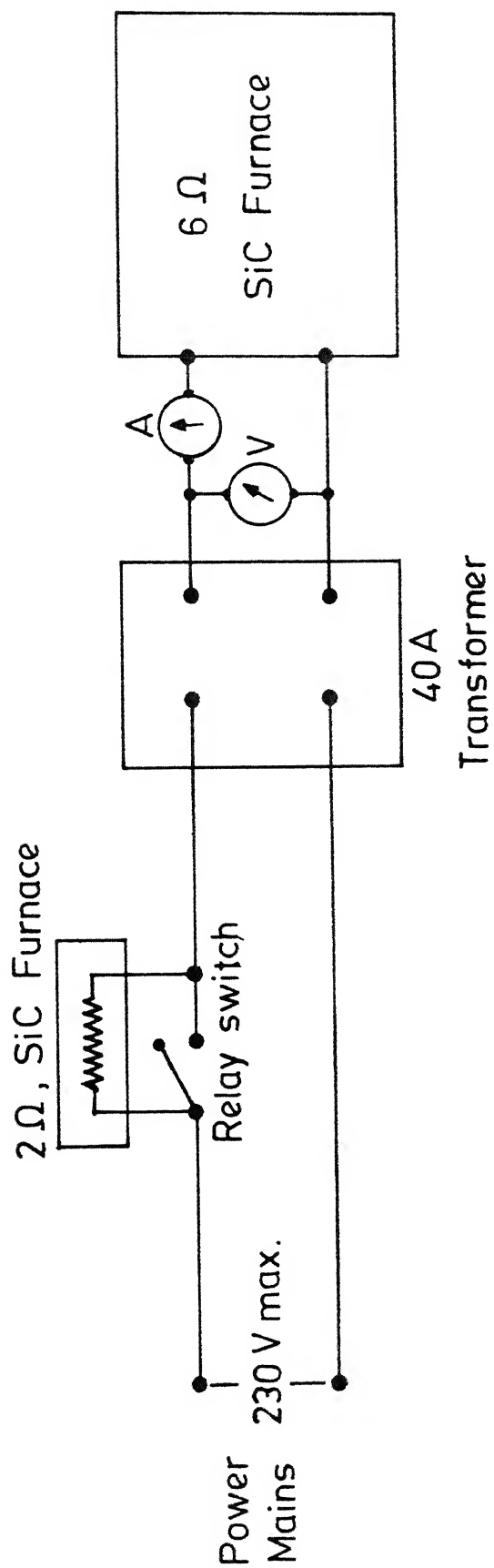


FIG. 4.2 SCHEMATIC CIRCUIT DIAGRAM FOR THE POWER SUPPLY TO THE SILICON CARBIDE FURNACE.

4.1.4 Gas train

The neutral atmosphere of argon was maintained in all the experiments to protect the melt from atmospheric oxidation. A calibrated capillary flowmeter was used to determine the flow rate of argon. The gas was purified by passing it through a calcium chloride tower to remove moisture and a copper gauge tube maintained at 260-300°C to absorb oxygen. The system for the flow of argon to the reaction tube is shown schematically in fig. 4.3.

4.1.5 Sulphur analysing set up

For analysing sulphur in the iron samples, the set up was made available in the laboratory itself. It consisted of 250 cc conical flask, B/34 glass joint, 250 cc separating funnel, glass tubes (6 mm. i.d.), 100 cc. measuring cylinder and 1500 watts hot plate. Titration set up consisted of a 50 cc burette and a 10 cc pipette. The set up is shown in fig. 4.4.

4.1.6 Manganese analysis

Analysis of manganese was done using the colorimetry method for which photoelectric colorimeter in the Analytical Laboratory of the Department was used.

4.2 Materials

4.2.1 Materials for melting

Solid pig iron samples weighing about 50 kg were obtained from Rourkela Steel Plant. They were suitably broken into

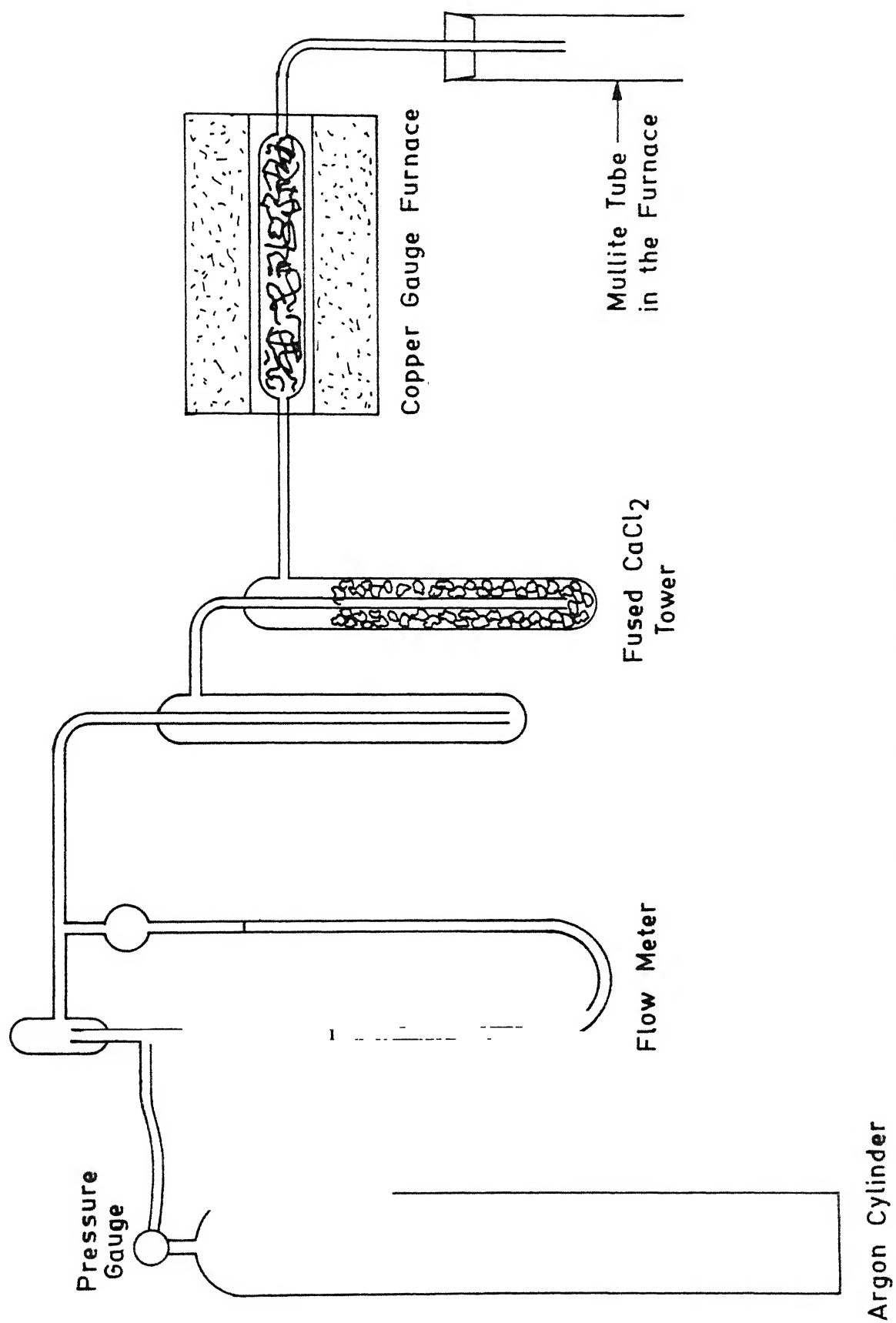


Fig. 4.3. Gas Train .

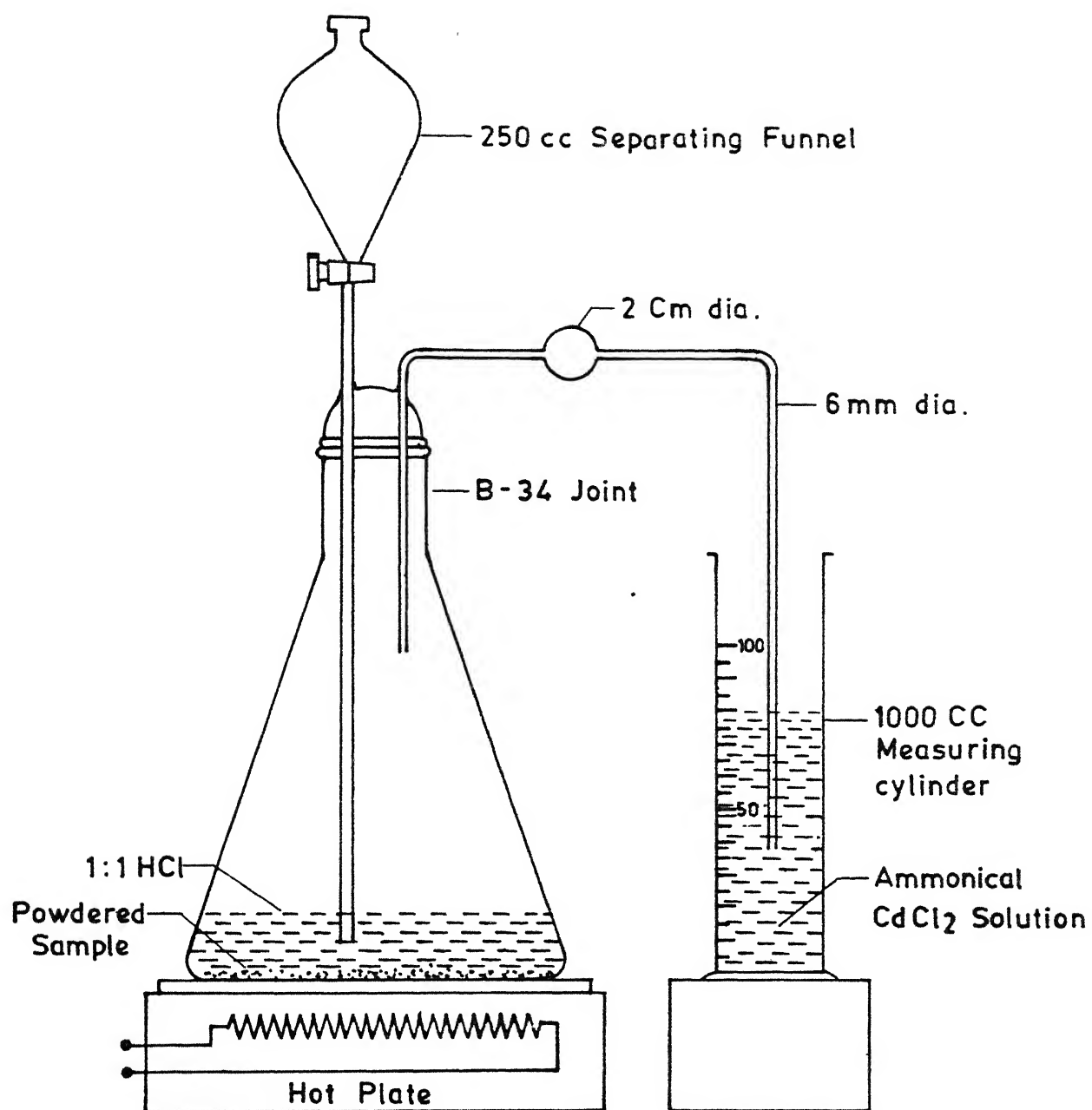


FIG. 4.4. SCHEMATIC SET UP FOR SULPHUR ANALYSIS.

small pieces for adding to the crucible. The pieces were washed with acetone before being used for the experiments. Manganese used was 99.9% pure in the powder form and obtained from USA. FeS used was of local make. Lime was obtained by the calcination of pure calcite in the laboratory at 1000°C for one hour.

4.2.2 Mullite crucibles

The crucible consisted of 2.8 cm i.d. and 60 cm. length mullite tube obtained from the Kumar Refractory and Co. The crucible rested on the bed of alumina powder or chips of the furnace tube as the case may be. It was held in vertical position by means of a clamp at the top.

4.2.3 Sampling tube

4 mm. dia and 1 mm. long quartz tubes were used for drawing metal samples. One tube could be used for drawing 5-6 samples.

4.2.4 Chemical reagents

HCl , HNO_3 , H_3PO_4 , CdCl_2 and ammonia solution used for chemical analysis of metal samples were of AR grade while potassium iodide, sodium thiosulphate and potassium periodate were of GR grade. Iodine used was of LR grade.

4.2.5 Standard steel sample

100 gms. of standard carbon steel sample supplied by British Chemical Standards No. 459/1 through their representatives, Laboratory Chemical Co. Calcutta, was used to calibrate the analysing equipment.

4.3 Experimental Procedure

4.3.1 Flowmeter calibration

The capillary flowmeter was calibrated using the soap bubble method. Here the flow rate was calculated by noting the time taken for a soap bubble to travel a fixed distance for different pressure drops of the flowmeter. The straight line graph thus obtained was used for calibration purposes.

4.3.2 Mn-S Interaction studies in liquid metal

The furnace was heated overnight by the passing current at the rate of 10-15 amps till the temperature reached 1200°C . The current was increased to around 20 amps and the furnace reached the temperature of 1400°C in about two hours. The mullite crucible charged with 100 gms of the blast furnace iron and other additions as required was lowered into the furnace. About 5 gm. of charcoal was also added to avoid the oxidation of the alloy and to ensure carbon saturation in the melt. The crucible was purged with argon gas before lowering it in the furnace and a steady flow of 3 cc per second of argon was maintained throughout the experiment, except for brief periods when the thermocouple was lowered for temperature measurements. The end of the refractory protection tube containing the thermocouple wires was kept just above the melt.

Sufficient and specified time was allowed for the melt to reach equilibrium. Continuous stirring of the melt was provided using a stainless steel rod. In the kinetic studies, the temperature was noted every minute except for the period when the sample was being taken out. The temperature of this period was found out by interpolation from temperature versus time plot. No stirring was done in these experiments.

The samples were collected by sucking in the liquid metal in a quartz tube using an aspirator. At a time 10-15 gms of the sample could be collected. The quartz tube was purged with argon prior to sampling to minimise oxidation of the melt by the entrapped air in the tube. In the equilibrium studies, sample was collected only after sufficient time had been given for equilibrium to be attained after every fresh addition or setting of new temperature.

4.3.3 Mn-S interaction studies in metal in the presence of lime

Pure calcium oxide prepared in the laboratory itself was used in the experiments. After the alloy had melted and attained equilibrium, a sample was collected. Then lime was added to the melt in powder form. In another experiment both lime and manganese were added after being thoroughly mixed with each other. Continuous stirring was done and samples collected at regular intervals till one hour after additions had been made. Experiments involving higher amounts of calcium oxide could not be done because of difficulty in sampling due to formation of a thick solid calcium oxide layer at the top. Similarly experiments with other

slag compositions having lower melting points were not made because of the uncertainty regarding the stability of the mullite tube in presence of molten slags containing CaO , Al_2O_3 and SiO_2 . At the end of the last experiment SiO_2 and Al_2O_3 were added to the crucible to check the stability of the tube in presence of such slags.

4.3.4 Chemical analysis of samples

The samples to be analysed were first powdered to minus 100 mesh size in a pestle and mortar. The analysis was obtained for manganese and sulphur.

4.3.4.1 Manganese

The analysis was done by colorimetric method using photoelectric colorimeter. Here 0.1 gm. of the steel sample was dissolved in 20 ml. of 1:3 nitric acid and boiled for 1-2 minutes to expel oxides of nitrogen. The solution was then dilute to 60 ml. and 5-10 ml. of syrupy phosphoric acid and 0.5 gm. of potassium periodate added. It was then boiled for one minute. The solution was cooled and made up to 100 ml. in a volumetric flask. In cases where the expected manganese content was above 1%, the solution was made upto 250 or 500 ml depending upon the expected manganese content. The colour of the diluted solution was then matched against standard solutions of 99.9% pure manganese and a standard steel sample with known manganese. A wavelength of 530 mμ was used in the colorimeter.

4.3.4.2 Sulphur

Sulphur was analysed by evolution technique in the laboratory. The set up was first tested for any leakage of gas. This was done by pressurizing the vessel with argon and then noting any pressure drop in the line with the supply of argon was cut off.

Then around 5 gms. of the powdered sample was transferred carefully to the conical flask. One gm. of CdCl_2 was dissolved in 60 ml. of water in a measuring cylinder and made ammonical. The exit end of the glass tube in the conical flask dipped in this CdCl_2 solution. 150 ml of 1:1 HCl was poured drop by drop in the conical flask. The sulphur in the alloy reacted with the HCl to form H_2S gas which was absorbed by the ammonical CdCl_2 solution to form a yellow precipitate of cadmium sulphide. Towards the end of the reaction, heat supply was increased to produce steam and flush out the remaining H_2S . When it was confirmed that the gas has been flushed out completely, the absorbing solution was cooled in an ice bath. The ice cold solution was acidified with 20 ml of concentrated hydrochloric acid. To the acidified solution 10 cc. of N/10 iodine solution was added and titrated against N/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution, using starch as indicator. It was followed by titration of N/10 iodine solution alone with N/10 $\text{Na}_2\text{S}_2\text{O}_3$ in each case. The difference in the two values of N/10 $\text{Na}_2\text{S}_2\text{O}_3$ amounts is the equivalent amount $\text{Na}_2\text{S}_2\text{O}_3$ solution consumed for sulphur in the sample. The percent sulphur is given by

$$\% S = \frac{0.16 Y}{X}$$

where Y is the amount of N/10 $\text{Na}_2\text{S}_2\text{O}_3$ consumed in millilitres and X is the weight of sample in grams.

CHAPTER VRESULTS5.1 Analysis of Original Rourkela Steel Plant Blast Furnace Iron and Standard Steel Sample

The Rourkela Steel Plant sample as obtained was analysed for sulphur and manganese and the following results were obtained.

Analysis No.	I	II	III	IV	Avg.
Sulphur (%)	0.035	0.029	0.033	0.031	0.032
Manganese(%)	1.54	1.6	-	-	1.57

The results were found to be within the limits of experimental error and average was calculated to get the percentages. Silicon and carbon were not analysed in the laboratory. Silicon can be taken to be around 1.4% which is typical of the Rourkela Steel Plant and carbon can be calculated by the following formula given by Young and Clark.⁽¹⁷⁾

$$[C] = 1.34 + 2.54 \times 10^{-3} T (^{\circ}C) - 0.35 P + 0.17 [Ti] - 0.40 (S) + 0.04 [Mn] - 0.30 [Si]$$

At different temperatures carbon will be given by :

Temperature	1400 ^o C	1300 ^o C	1200 ^o C
[%C]	4.42	4.17	3.91

Here phosphorous has been taken as 0.30% and titanium as zero.

The BCS standard steel sample was also analysed for sulphur and the following results were obtained :

Analysis No.	I	II	Avg.	Reported
[S]	0.051	0.053	0.052	0.057

5.2 Stepwise Change in the Melt Temperature at Constant Manganese Addition to the Melt

Three sets of experiments were done involving stepwise cooling and heating of the blast furnace iron at constant manganese additions to the melt. It took almost one hour for the temperature to reach the new value after being set. The details of the experiments and results of analysis of sulphur and manganese in the samples are given in Table 5.1.

5.3 Stepwise Additions of Manganese at Constant Temperature

Heat No. 5 involved stepwise addition of manganese from 0% to 4% at one percent intervals at the temperature of 1400°C. The samples were taken after allowing 2-3 hrs. for equilibrium to reach after the addition of manganese. The results of sulphur and manganese analysis are given in Table 5.2.

5.4 Cooling of Melt at Different Cooling Rates

Two sets of experiments were done to study the effect of cooling rate on the sulphur levels in the melt. While in

Table 5.1

Details of Experiment and Results of Stepwise Changes in the melt temperature at constant manganese addition to the melt.

Heat No.	Additions			Sample No.	Holding Time (hrs.)	Actual Temp. (°C)	Amount Taken out (g)	S (%)	Mn (%)
	Blast Furnace Iron(g)	Mn (g)	FeS (g)						
2	100	-	-	21	2	1400	25	0.033	1.67
				22	2	1305	7	0.036	1.6
				23	1:45	1220	4	0.025	1.6
3	100	-	2.8	31	2	1405	9	0.127	1
				32	2	1300	10	0.08	0.86
				33	2	1206	14	0.036	0.75
				34	2:15	1310	14	0.076	0.83
4	100	2	2.8	41	2	1405	13	0.058	2.38
				42	2:30	1300	6	-	2.38
				43	2:30	1200	11	0.014	2.38
				44	2	1300	13	0.028	2.38

Table 5.2

Experimental Details and Results of Stepwise Addition
of Manganese at Constant Temperature.

(Heat No. 5)

DETAILS : Input Materials : Blast Furnace Iron:100 gm.+2.8 g FeS
Temperature : 1400°C.

Sample No.	Mn added (g)	%Mn Addition	Amount Taken out (g)	Temp. (°C)	Holding Time (hrs.)	S (%)	Mn (%)
51	0	0	5	1400	2	0.19	1.08
52	1	1.05	10	1405	2:15	-	1.33
53	0.7	1.98	6	1400	2:45	0.069	1.85
54	0.7	3.04	8	1400	1:45	0.055	2.27
55	0.4	3.94	23	1400	2:00	0.051	2.90

heat 7 the power supply to the furnace was completely cut off in heat No. 8 the power was supplied to the furnace at the reduced rate of 10-12 amps throughout the period of cooling. In both the experiments the starting material was the blast furnace iron with one percent sulphur addition and the starting temperature 1400°C . Temperature was measured continuously with time and the temperature for the period during sampling found from the plot of temperature versus time as shown in fig. 5.1. The result of the two experiments is given in Table 5.3.

5.5 Effect of Lime Additions on Mn-S Interactions

Heat nos. 9 and 10 were used to study the role of manganese on the desulphurising power of lime addition. The melt was kept at 1400°C and the samples taken with time for a period of one hour. The details of experiment and results are given in Table 5.4.

5.6 Preparation of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag in mullite crucible

At the end of heat No. 10, 10 gms. of quartz and 5 gm. of silica were added to the mullite crucible to prepare a $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag in 2:2:1 ratio. The system was left at 1400°C for one hour. When the tube cooled down, the tube was broken and the attack of slag on the mullite tube was studied. It was found that the slag formed had reacted with the tube walls but the reaction was not even throughout the tube. At some

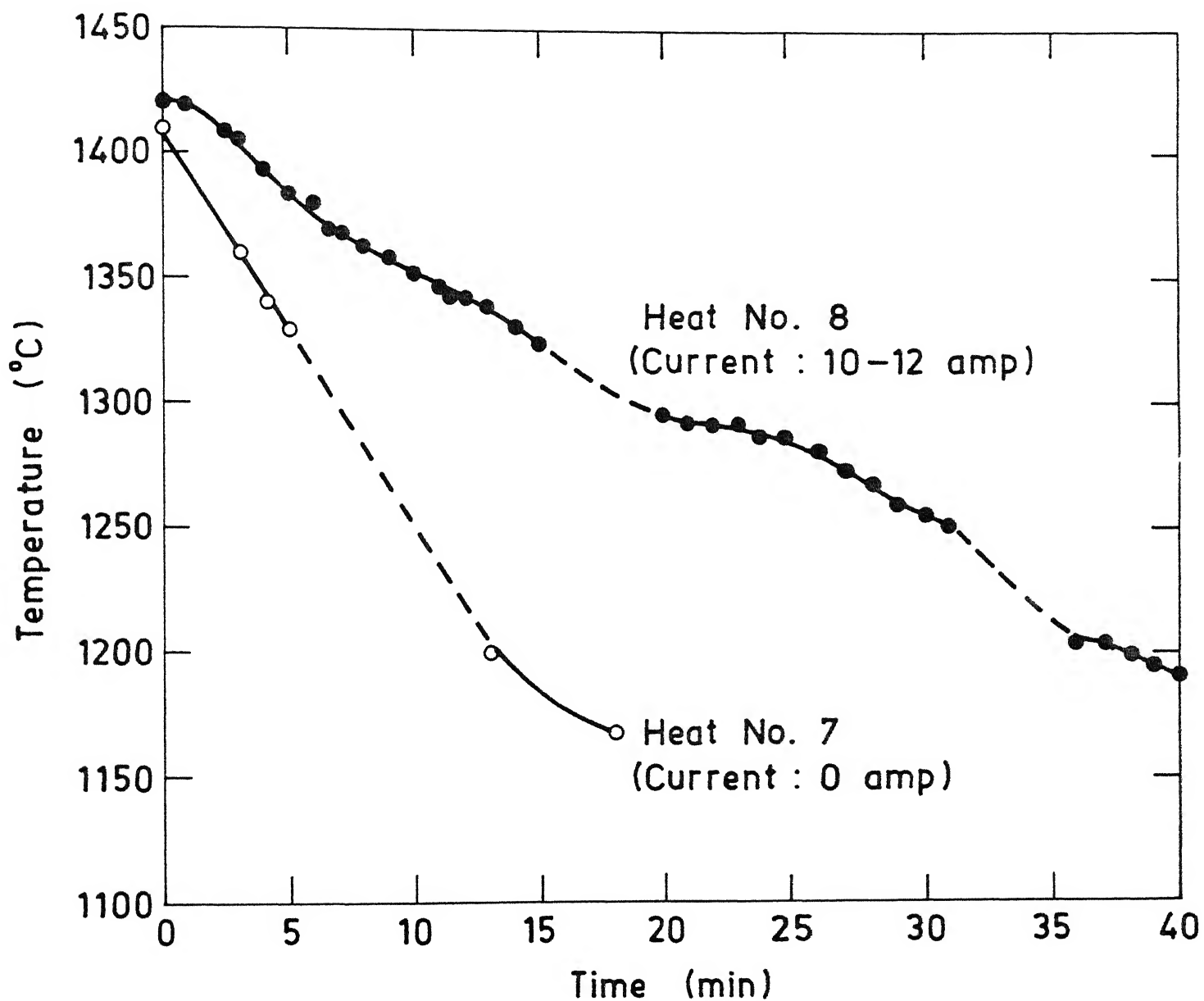


Fig. 5.1. Variation of temperature with time at different cooling rates in heat no. 7 and 8.

Table 5.3

Experimental Details and Results of Cooling of Melt
at Different Cooling Rates.

Heat No.	Input Materials		Current (amps)	Sample No.	Time after setting of current (min)	Temp (°C)	S (%)	M (%)
	Blast Furnace Iron (g)	FeS (g)						
7	100	2.8	0	71	0	1410	0.112	0.98
				72	6.45	1305	0.072	0.86
				73	13	1205	-	0.79
8	100	2.8	10-12	81	0	1420	0.119	0.94
				82	17.5	1310	0.075	0.81
				83	32.5	1235	0.026	0.70

Table 5.4

Details of Experiment and Results of Effect of Lime Additions on Mn-S Interactions.

Heat No.	Input Material				Sample No.	Time after CaO addition (min)	Temp. (°C)	S (%)	Mn (%)
	Blast Furnace Iron (g)	FeS (g)	Mn (g)	CaO (g)					
9	100	2.8	-	10	91	0	1400	0.117	0.94
					92	48	1400	0.090	1.1
					93	60	1400	0.094	1.14
10	100	2.8	2	10	101	0	1400	0.120	0.98
					102	20	1400	0.049	1.32
					103	42	1400	0.041	1.75
					104	62	1400	0.041	2.03

places about 60% of the tube wall had reacted while in other places the reaction had hardly begun. If the tube would have been left at 1400°C for some more time the slag might have reacted throughout the tube cross-section at some places.

CHAPTER VIDISCUSSION

The results of experiments with stepwise changes in temperature of the melt show that the sulphur level decreases with decrease in temperature of the melt ~~show that sulphur level decreases with decrease in temperature~~ in agreement with the results first reported by Morris⁽⁶⁾ and Olsen⁽²⁰⁾ and later confirmed by Pattjoshi⁽¹⁾. The present results are compared with those of the investigators in the fig. 6.1. In the present work silica was present which could affect the results in the following manner :

1. Change in solubility of carbon in iron and hence the lowering of f_s value.
2. Increase in f_s due to the presence of silicon in the melt.

Now,

$$\log f_s = e_s^{Si} [\%Si] + e_s^C [\%C] - 0.0282 [\%S]$$

$$\begin{aligned} \therefore \log f_s &= \Delta[\%Si] e_s^{Si} + e_s^C \Delta[\%C] \\ &= \Delta[\%Si] [e_s^{Si} - 0.3 \times e_s^e] \end{aligned}$$

Pattjoshi⁽¹⁾ had calculated the values of e_s^C at 1400°C as 0.1698 using regular solution model. Taking the value of e_s^{Si} as 0.066 as given by Eliot et al⁽⁵⁾, we get

$$\log f_s = 0.015 [\%Si]$$

Therefore, presence of 1.4% silicon in the metal leads to an increase in f_s by just 4% only. Hence it would affect the

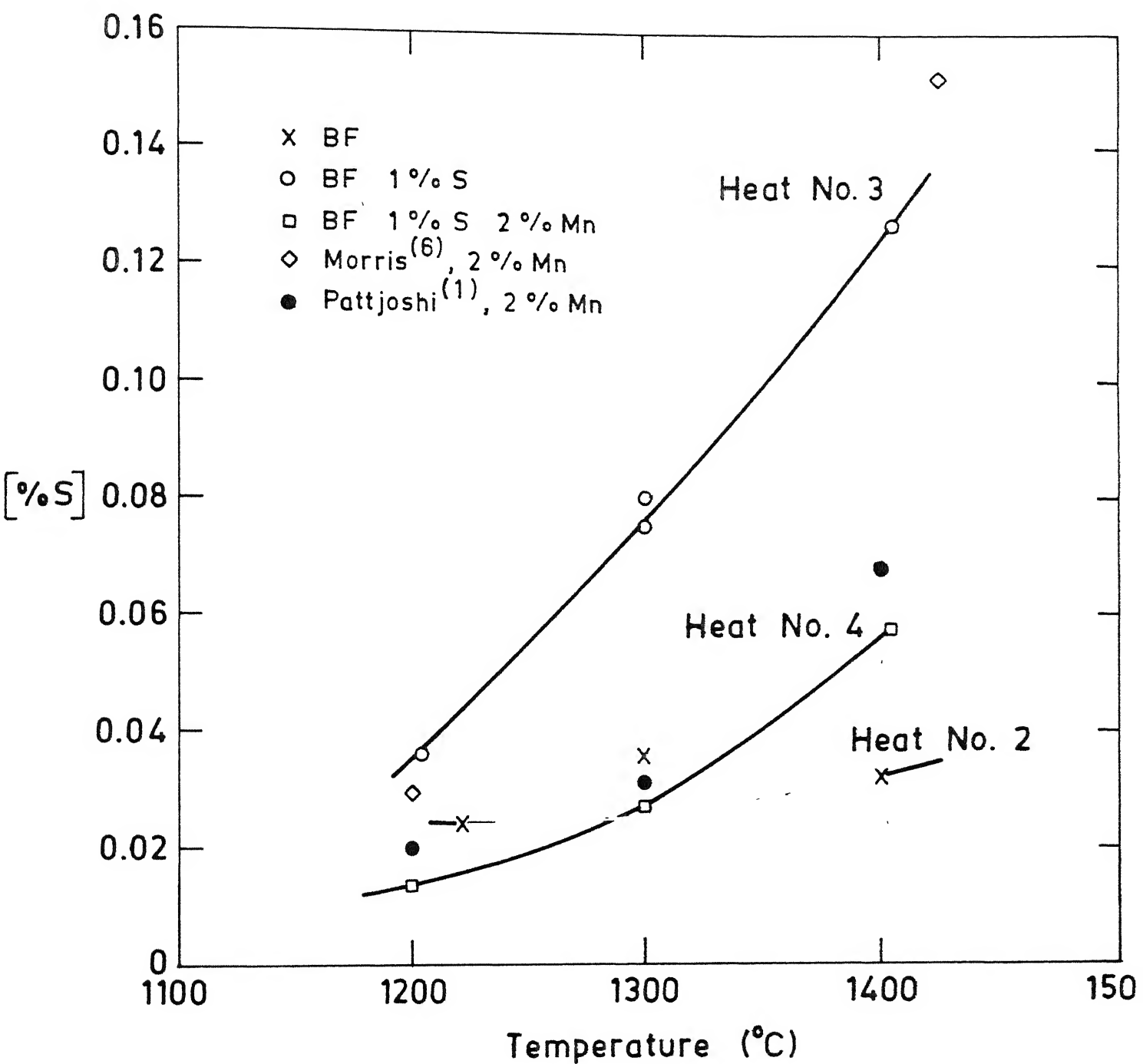


Fig. 6.1. Variation of sulphur content in the melt with temperature.

results marginally and within the limits of experimental error. This is seen by comparing the results of the present work with that of Pattjoshi's⁽¹⁾ data on melts without silicon.

Similarly the results of stepwise addition of manganese at 1400°C show that the solubility of sulphur in the melt decreases with increase in manganese level of the melt. The results of all the experiments done at 1400°C are compared with those of Morris⁽⁶⁾ and Pattjoshi⁽¹⁾ in fig. 6.2. Theoretically, the sulphur level will be given by the following :

$$\underline{\text{Mn}} + \underline{\text{S}} = \text{Mn S(s)} ; \log K = \frac{8191}{T} - 4.99 \quad \dots (6.1)$$

$$\text{Therefore, } [\text{S}] = \frac{a_{\text{MnS}}}{[\text{Mn}] f_{\text{Mn}} f_{\text{S}} \cdot K_{1400}}$$

f_{Mn} is taken to be around 0.8 . Value of f_{S} does not change much with change in manganese level. So the solubility product of manganese and sulphur should remain constant at a given temperature. This is seen in Table 6.1 where except for two values at 1400°C, more or less constant values are obtained. A graph of $\log [\text{Mn}]$ versus $\log [\text{S}]$ plotted in fig. 6.3 is a straight line as predicted by theory. At 1300°C and 1200°C, the curve shifts towards left as determined by Morris⁽⁶⁾, Oelsen⁽²⁰⁾ and Pattjoshi⁽¹⁾.

The results of different rates of undisturbed cooling of the melt are very interesting. They show that the drop in sulphur is quite rapid with decrease in temperature and the

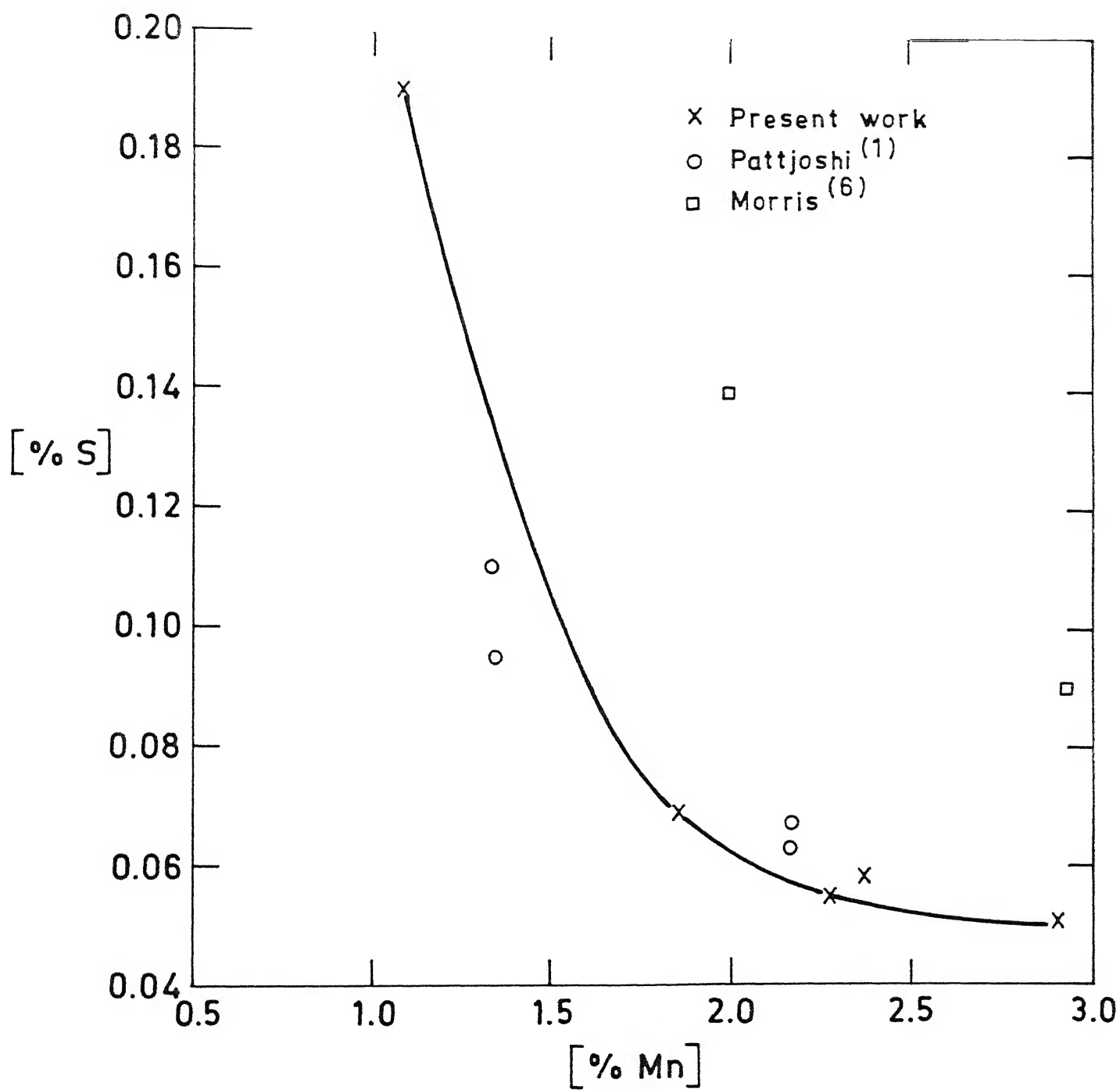


Fig. 6.2. Effect of manganese on sulphur content of metal at 1400 °C.

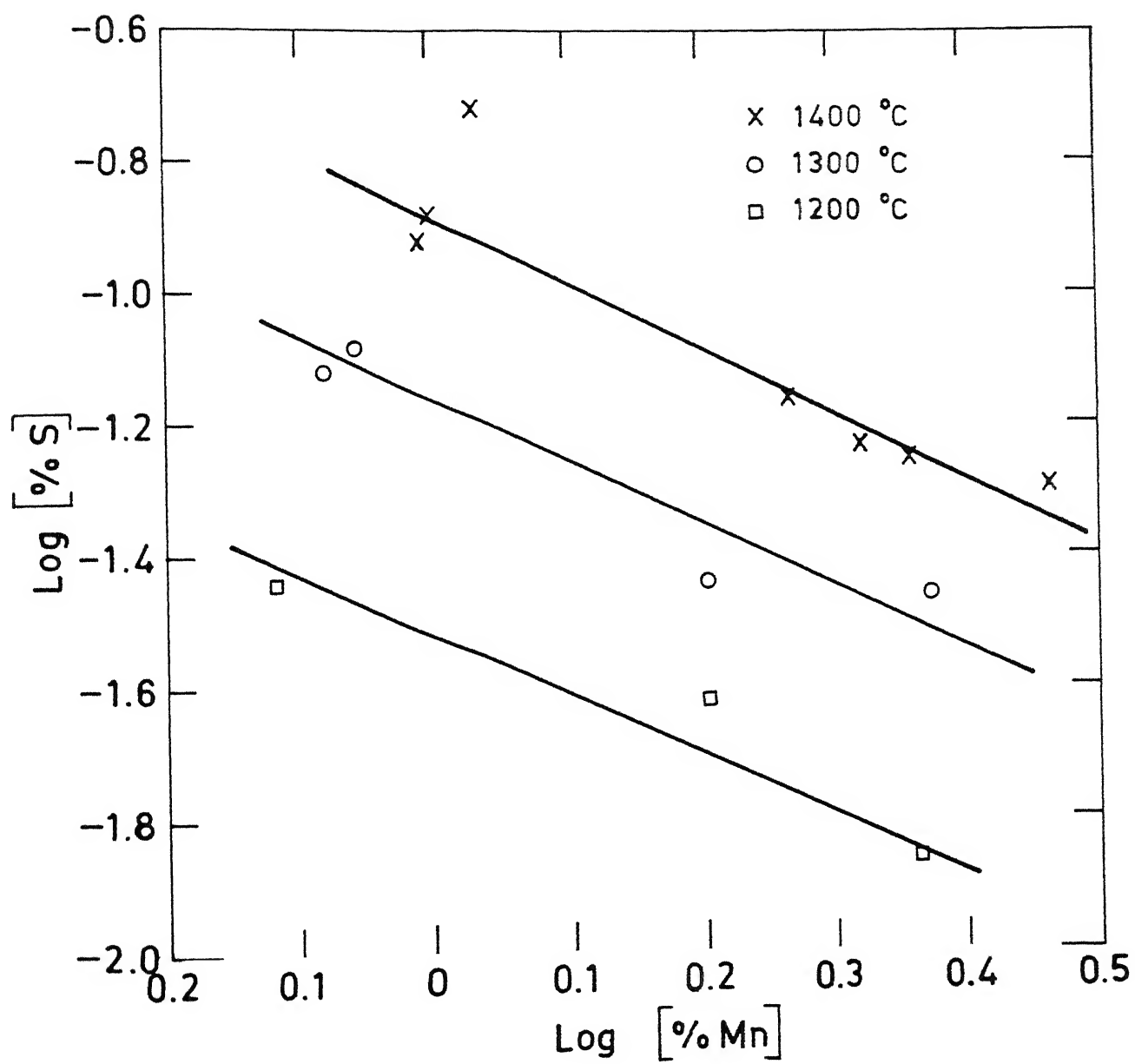


Fig. 6.3. Variation of log [% S] with log [% Mn].

Table 6.1

Values of [%Mn] x [%S]

1400°C		1300°C		1200°C	
Sample No.	[%Mn] x [%S]	Sample No.	[%Mn] x [%S]	Sample No.	[%Mn] x [%S]
51	0.205	32	0.069*	23	0.04*
52	0.127	34	0.063*	33	0.027*
53	0.125	44	0.066*	43	0.033*
54	0.125	22	0.058*		
55	0.146				
71	0.109*				
81	0.111*				
91	0.11*				
101	0.117*				

* : Obtained from results obtained at these temperatures in other heats.

rate of cooling apparently does not have much effect on the results as shown in fig. 6.4. As temperature decreases the solubility product of manganese and sulphur should decrease. The sulphur content is usually below 0.1%, hence corresponding change in manganese will be very marginal. The reaction between manganese and sulphur i.e. reaction 6.1 must be occurring throughout the depth of the bath with the lowering of temperature and manganese sulphide tends to float out to the top of the bath due to its lower density. It is likely that manganese and sulphur in the melt remain at equilibrium with respect to MnS phase at all temperatures during cooling.

It may therefore follow that in an industrial process there will be a decrease in sulphur level of the hot metal in presence of manganese when the ladle containing metal is transported from the blast furnace to the mixer. It may take 1-2 hour for the transfer during which temperature may drop around 100-200°C. The data of the Rourkela Steel Plant in the past show that the sulphur content of the metal is lowered from 0.06% to 0.04%. Also, the mixer slag is known to be rich in sulphur.

There were real difficulties in carrying out experiments with lime additions in the bath. The presence of solid lime powder at the top created problems in drawing samples from the bath. Results show that in about one hour or so, there is around 15-20 percent drop in sulphur content when 10% lime is added with manual stirring being done with a stainless steel rod

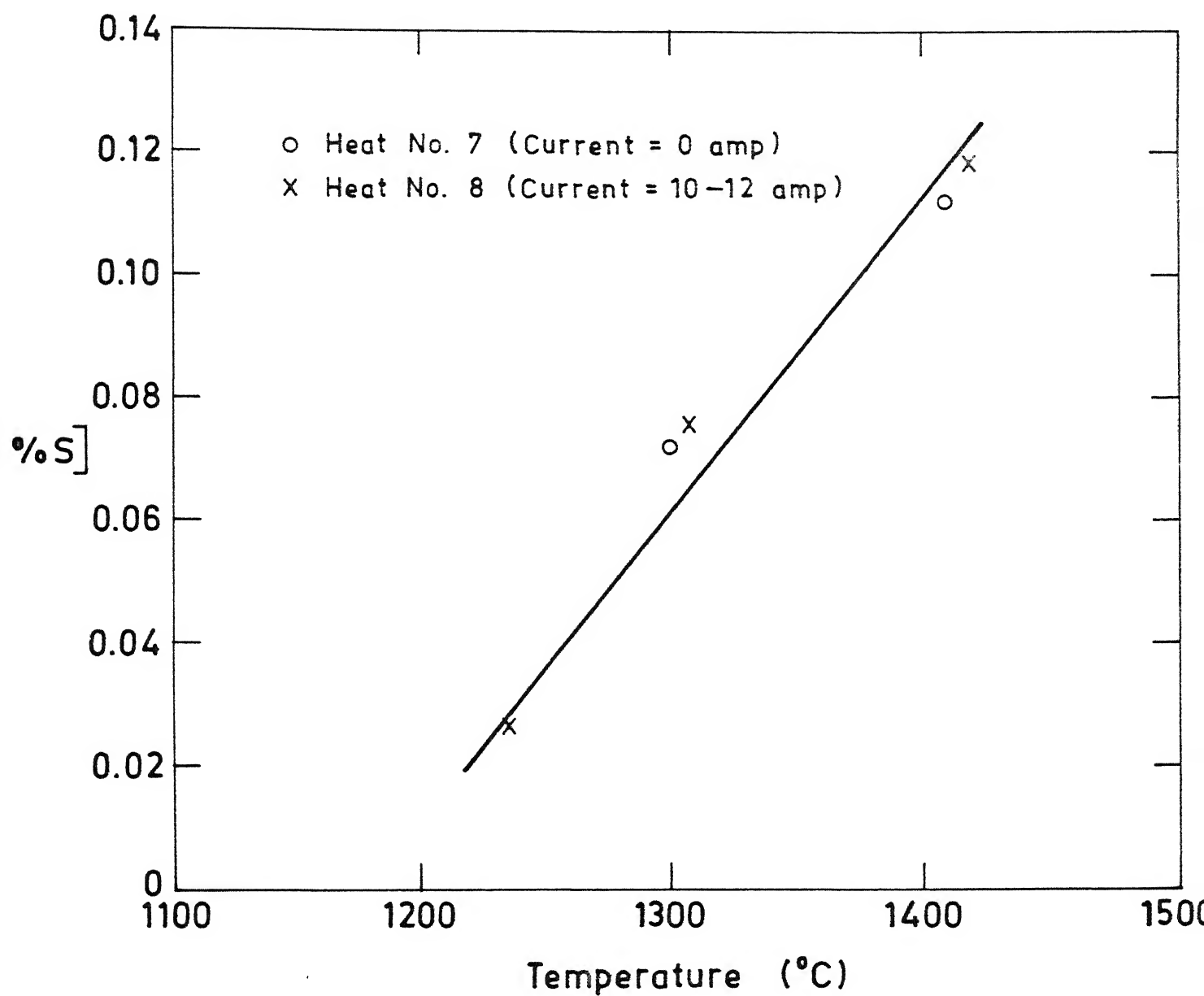
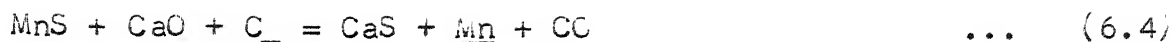


Fig. 6.4. Effect of cooling on sulphur content of metal.



The change in the Mn content of metal due to this reaction will be too small to cause any further removal of S as MnS . The further reduction of sulphur will occur only by reaction 6.3 which is shown to be slow in absence of sufficient stirring of the bath.

In the experiments involving $\text{CaO-Al}_2\text{O}_3\text{-SiC}_2$ slag formation in a mullite crucible it was found that the slag had reacted with the crucible as much as 60% of the thickness of the crucible at some places in 60-90 minutes of heating. Thus the crucible might be suitable for studies just upto one hour periods. Prolonged equilibrium studies involving such slags may be carried out in the graphite crucibles. The present facilities in the laboratory did not allow these investigations to be carried out.

CHAPTER VII
SUMMARY AND CONCLUSIONS

Thermodynamics of sulphur reactions and desulphurising powers of various blast furnace and steel making slags have been investigated by many workers by equilibrating the melt with known H_2/H_2S ratio or with a known quantity and composition of slag at a fixed temperature. Here an attempt was made to study manganese-sulphur interactions in blast furnace iron obtained from Rourkela Steel Plant in the temperature range of 1200-1400°C which is the usual temperature occurring during the transit of metal from the blast furnace to the mixer.

A silicon carbide furnace was used for carrying out the experiments. The experiments were done in a mullite crucible under argon atmosphere and samples were taken with the help of quartz tubes. Calibrated thermocouples were used to measure the temperature just above the melt. Analysis of samples was done for sulphur by the evolution technique and of manganese by colorimetric method.

Four categories of experiments were carried out. Stepwise cooling and heating of the blast furnace iron was done with 1% sulphur addition and with and without 2% manganese addition.

Samples were collected at 1400, 1300, 1200 and 1300°C, after sufficient time was given for equilibrium to be attained. Studies on stepwise addition of manganese to blast furnace iron with 1% sulphur addition was done at 1400°C for 0%, 1%, 2%, 3% and 4% manganese addition. Another set of experiments involved

studying of the undisturbed melt consisting of blast furnace iron with one percent sulphur addition subject to two different cooling rates. Lastly, the effects of lime addition on desulphurisation was also studied by addition of 10% lime to melts with and without manganese additions.

The results of stepwise cooling and heating showed that there was reduction in sulphur content of the melt with decrease in temperature. This agreed with the findings of other investigators.

The results of stepwise addition of manganese showed that the sulphur level in the melt decreases as the manganese level increases. Also the solubility product of sulphur and manganese was found to be almost constant as predicted by the thermodynamical calculations. The experiments on effect of cooling rates confirmed that sulphur level decreases with decrease in temperature. The cooling rate apparently did not have any effect on sulphur content. The studies on effect of lime addition reveal that both CaO and Mn react independently to reduce sulphur levels in iron. The effect of lime was limited in the present work because of slower kinetics due to insufficient stirring. The study on viability of mullite crucible for slag-metal equilibrium investigations showed that while it was suitable for short duration studies, for longer periods graphite crucibles should be made use of.

CHAPTER VIII

SUGGESTIONS FOR FURTHER WORK

As already suggested earlier, the next step should be the study of slag-metal equilibrium using graphite crucibles. The studies should be done for different slag compositions and quantities. Both synthetic and actual blast furnace slags should be made use of. The study will help in understanding the actual phenomenon occurring in the industry and lead to efficient desulphurisation of metal at lower costs.

Efforts should be made for preparation of manganese sulphide and iron sulphide in the laboratory itself rather than procuring locally to avoid any contamination. Studies by addition of MnS to iron-carbon melt should be done to give an independent confirmation of manganese sulphur equilibrium in the Fe-C-Mn-S melt.

Further experiments may be planned for equilibrating the Fe-C-Mn melt with known H_2/H_2S ratio at fixed temperatures. H_2/H_2S ratio of H_2 and H_2S gas mixture will correspond to a particular sulphur concentration in the melt at equilibrium and this in turn will correspond to a particular manganese content of the metal. The final manganese content of the alloy melt can thus be compared with the theoretical value of manganese-sulphur equilibrium calculations. The starting manganese in the melt must be kept greater than the equilibrium value for such experiments.

REFERENCES

1. Pattjoshi, A.K., 'Manganese-Sulphur Interactions in Iron-Carbon Alloys', Ph.D. Thesis, I.I.T., Kanpur (1985).
2. Banya, S. and Chipman, J., 'Sulphur in Liquid Iron Alloys : I, Binary Fe-S', Trans. Met. Soc., AIME, 242 (May 1968) p. 940-946.
3. Sherman, C.W. and Chipman, J., 'Activity of Sulfur in Liquid Iron and Steel', Trans. AIME, Journal of Metals (June 1952) p. 597-602.
4. Morris, J.P. and Buehl, R.C., 'Effect of Carbon on the Activity of Sulphur in Liquid Iron', Trans AIME, Journal of Metals, 188 (Feb. 1950) p. 317-322.
5. Eliot, J.F., Gleiser, M. and Ramakrishna, V., 'Thermochemistry of Steel Making, Vol. 2, Reading Mass., Addison Wesley (1963) p. 525.
6. Morris, J.P., 'Effect of Manganese on the Activity of Sulphur in liquid Fe and FeC Alloys', Trans. AIME, Journal of Metals (Sept. 1952). p. 939-940.
7. Hatch, G.G. and Chipman, J. 'Sulphur Equilibria between Iron Blast Furnace Slag and Metal'. Met. Trans. (April 1949).
8. Venkatesh, A.S. and Bell, H.B., 'Sulphur Partition between Slag and Metal in the Iron Blast Furnace', JISI, 207 (Aug. 1969) p. 1110-1113.
9. Kalyanram, M.R., Marfarlane, T.G. and Bell, H.B., JISI, 195 (1960) p. 58.

10. Tsao, T. and K. Tayaama, H.G. 'Sulphur Distribution between Liquid Iron and $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ Slags used for Ladle Refining' Trans. of Iron and Steel Inst. of Japan, 26 (1986) p. 717-723.
11. Filer, E.W. and Darken, L.S., 'Equilibria between Blast Furnace Metal and Slag as determined by Remelting', Trans. AIME Journal of Metals (March 1952) p. 253-257.
12. Turkdogen, E.T. Kor, G.J., and Fruchan, R.J. 'Studies of Blast Furnace Reactions' Ironmaking and Steelmaking. 6 (1980) p. 268-280.
13. Biswas, A.K., 'Principles of Blast Furnace Iron Making', Cootha Publishing House, Brisbane (1981), p. 92.
14. Grant, N.J., Galling, U. and Chipman, J. 'Effect of Manganese and its Oxide on Desulphurization by Blast Furnace Type Slags', Trans. AIME, Journal of Metals (Aug. 1951) p. 666-671.
15. Grant, N.J., Dauding, J.W., and Murphy, R.J. 'Manganese as an indicator of Blast Furnace Slag Oxidation and Desulphurizing Power' Trans. AIME, Journal of Metals (Nov. 1953) p. 1451-1454.
16. Froberg, M.G., Nilas, A. and Kapoor, M.L. 'Kinetics of Sulphur Transfer between Iron Melts and Metallurgical Slags.' Proceed. ICSTIS, Suppl. Trans. ISIJ 11 (1971) p.495-500.
17. Young, D.J. and Gripps Clark, C.J. 'Sulphur Partition in Blast Furnace Hearth'. Ironmaking and Steelmaking 5 (1980) p. 209-214.

18. Sherman, C.W., Elvander, H.I. and Chipman, J., Trans. AIME, 108 (1950) p. 334.
19. Morris, J.P. and Williams, A.J. Trans. ASM (1949), 41, p. 1425.
20. Oelsen, W., Stahl and Eisen 68 (1948) p. 175-186.
21. Haastert, H.P., Nellermeier, H. and Peter, K.H., 'Operational Aspects of the Injection Process for Desulphurization of Hot Metal', Iron and Steel Engineer (Oct. 1975). p. 71-77.

ME-1986-M-KUM-LAB